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Contents

Vol. 35, No. 1, 2000

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Noble Metals in Sulfide Assemblages from Deep Sectors of the Active TAG Mound (Mid-Atlantic Ridge, 26°08' N) <i>N. N. Mozgova, Yu. S. Borodaev, T. V. Stepanova, G. A. Cherkashev, and E. A. Zhirnov</i>	1
Geochemistry of Rare Earth Elements in Micro- and Macronodules from the Pacific Bioproductive Zone <i>A. V. Dubinin and V. N. Sval'nov</i>	19
Some Features of the Evolution of Carbonate Accumulation in the Earth's History: Communication 1. Evolution of the Intensity, Mechanism, and Setting of Carbonate Accumulation <i>V. G. Kuznetsov</i>	32
Organic Matter in Oligocene Maikop Sequence of the North Caucasus <i>M. L. Saint-Germes, O. K. Bazhenova, F. Baudin, N. I. Zaporozhets, and N. P. Fadeeva</i>	47
Mesozoic Carbonaceous Clayey Formations of the Central Russian Plate: The Problem of Their Ore Potential <i>A. A. Konstantinovskii and A. G. Volchkov</i>	63
H and O Isotopic Compositions of Layered Silicates in Metasomatites from the Gai Zn–Cu Massive Sulfide Deposit, Southern Urals <i>A. I. Grabezhev, B. G. Pokrovskii, F. P. Buslaev, V. V. Zaikov, and G. N. Pshenichnyi</i>	70
A New Type of Open Fracturing in the Rocks <i>V. P. Potapov and N. P. Dozmarova</i>	76

Critics

A New Genetic Model of Phosphorite Formation (Critical Analysis of Publications by V.N. Kholodov and R.K. Paul) <i>E. L. Shkol'nik, E. A. Eganov, A. S. Sokolov, and A. F. Georgievskii</i>	80
Strange Inaccuracies (A Reply to Critical Comments by E.L. Shkol'nik <i>et al.</i> , "A New Genetic Model of Phosphorite Formation") <i>V. N. Kholodov and R. K. Paul</i>	83

Chronicle

The Third Ural Regional Lithological Meeting <i>P. P. Timofeev, V. P. Alekseev, and L. V. Anfimov</i>	86
The First All-Russia Lithological Workshop of Young Scientists <i>P. P. Timofeev, A. E. Khardikov, and O. S. Ponomarenko</i>	87
In Memory of N.A. Lisitsyna	89
The Centenary of M.P. Fiveg	91

Noble Metals in Sulfide Assemblages from Deep Sectors of the Active TAG Mound (Mid-Atlantic Ridge, 26°08' N)

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Abstract—Primary sulfides from cores of holes 957M, 957C, and 957H drilled during the ODP Leg 158 on the active hydrothermal TAG mound (Mid-Atlantic Ridge, 26°08' N) were examined for the concentration of several elements. Based on 262 microprobe analyses, it has been established that the sulfides are characterized by an extremely heterogeneous distribution of noble metals (Au, Ag, Pt, and Pd) and several associated elements (Hg, Co, and Se). Noble metals are arranged in the following order in terms of decreasing abundance, i.e., concentration level above the detection limit (the number of analyses containing the specific element is given in parentheses): Au (65), Ag (46), Pt (21), and Pd (traces). The associated trace elements make up the following series: Co (202), Hg (132), and Se (49). Main carriers of the “invisible” portion of noble metals are represented by pyrite (Au, Hg), marcasite and pyrite (Ag, Co), sphalerite and chalcopyrite (Pt, Pd), and chalcopyrite (Se). The noble metal distribution in sulfides reveals a lateral zonality: the maximal concentration and abundance of Au in chalcopyrite (or Pt and Ag in chalcopyrite and pyrite) increase from the periphery (Hole 957H) to the center (holes 957C and 957M) of the hydrothermal mound, while the Au distribution in pyrite displays a reversed pattern. The Co distribution increases with depth. This work discusses the vertical zonality in the distribution of elements mentioned above and their response to the evolution of ore genesis.

A large active sulfide mound was discovered in 1985 within the hydrothermal Transatlantic Geotraverse (TAG), Mid-Atlantic Ridge, 26°08' N (Rona *et al.*, 1986). In terms of dimension (Fig. 1), the TAG mound is comparable with sulfide deposits in Cyprus, Oman, and other ophiolite regions (Fouquet *et al.*, 1998). The total mass of hydrothermal material in this edifice is estimated at 3.9 Mt (2.7 Mt in the mound proper and 1.2 Mt in the underlying stockwork zone). The pyrite reserve is estimated at 2.3 Mt, and the concentration of major metals is as follows: Cu 2.83 wt %, Zn 0.42 wt %, Pb 65 g/t, Ag 14 g/t, and Au 534 mg/t (Hannington *et al.*, 1998). This edifice represents the first mound discovered in mid-oceanic rifts with a low spreading rate (≤ 2 cm/yr). Owing to the large size, maturity, and prolonged hydrothermal activity, the TAG mound became an attractive object for several international research programs. Samples collected from this site were used for deciphering the mineralogy and geochemistry of hydrothermal formations, including the concentration of noble metals (Crocket, 1990; Hannington *et al.*, 1988, 1991; Krasnov *et al.*, 1995; Rona *et al.*, 1986, 1993a, 1993b; Thompson *et al.*, 1988; Tivey *et al.*, 1995; and others).

In 1994, 15 holes were drilled under the Ocean Drilling Program (ODP) to study the internal structure

of the TAG mound (Fig. 2). The deepest hole reached a level of 125.7 mbsf. The holes were drilled at five sites (Fig. 2, TAG 1–TAG 5) to obtain comprehensive information about the horizontal and vertical structure of the mound. Results based on the study of cores were first published in the preliminary report (Humphris *et al.*, 1994). The problem of mineralogy and geochemistry received considerable attention in the final report (Herzig *et al.*, 1998b). The ample analytical material in these reports included data on Au and Ag concentrations in bulk samples, based on cores from different holes within one sector.

This work presents results of a comprehensive microprobe study of the concentration of Au, Ag, Pt, Pd, and several associated elements in sulfide minerals from core samples of the TAG mound. We have attempted to elucidate the noble metal distribution in its deep sectors and decipher specific features of the response of these metals to the evolution of ore genesis.

GENERAL FEATURES OF THE TAG MOUND

The geological setting of the active TAG mound is briefly described here on the basis of several publications mentioned above. The mound is located approximately 2.5 km to the east from the axial sector of the rift

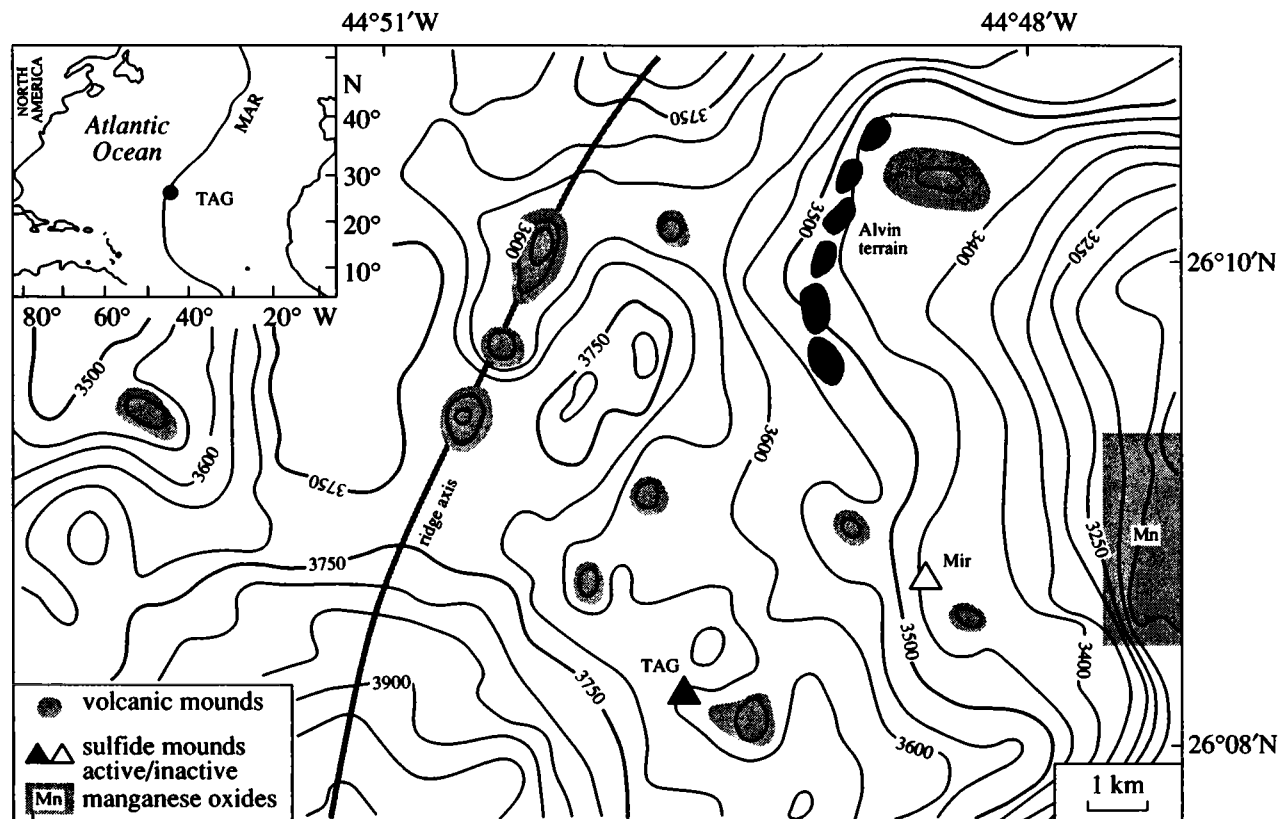


Fig. 1. Schematic position of the hydrothermal TAG mound, modified after (Rona *et al.*, 1993b).

valley floor at a depth interval of 3630 and 3670 m (Fig. 1). It partially overlaps the northwestern margin of a pillow lava sheet covered by carbonate sediments up to 1 m thick. The ore mound and volcanic edifices are confined to the intersection of small fractures that are parallel or perpendicular to the valley axis.

The mound is characterized by steep slopes and a rounded (in plan) structure with a diameter of approximately 200 m and height of up to 50 m (Fig. 2). The active hydrothermal activity is concentrated in two areas: (1) the central assemblage of black smokers and (2) the Kremlin sector, thus named because of the cupola-type form of white smokers. The first sector is situated 25 m to the northwest from the mound center, while the second sector is located 70 m to the southeast from the center. The central cone-shaped assemblage (height up to 20 m and diameter 50 m) is crowned with a group of chimneys, where high-temperature (360–366°C) fluids are mixed with seawater to precipitate sulfides of Cu and Fe (mainly chalcopyrite) and anhydrite. The tapered chimneys are up to 15 m high. The mound summit (diameter 10 m) is hidden under vigorous fluid effusions (the flow rate reaches several meters per second) saturated with fine mineral particles. A less intense black smoke is emitted from fissures around the main cone.

In white smokers of the Kremlin sector, fluid flows are characterized by a lower temperature (273–301°C) and lesser flow rate (<1 m/s). Here, sulfides of Fe and Zn, along with silica, are accumulated. The chimneys are generally small (1–2 m) and include inactive bodies. The gentle sector between black and white smokers is covered with sulfide debris (dimension ranging from large boulders to fine sand), chimney fragments, and iron oxide crusts. Low-temperature fluids are diffused through a network of cracks. Crusts of sulfides and corroded massive anhydrite are encountered near the central group of black smokers. Mound slopes are covered with sulfide debris with rare fragments of altered basalt.

Based on the radiometric dating of hydrothermal product samples, episodic activity of the mound started at least $40\text{--}50 \times 10^3$ years ago and is related to the pulsating supply of lava flows from an adjacent volcanic center that served as a heat source (Lalou *et al.*, 1993; Rona *et al.*, 1993b).

The mound surface is mainly composed of sulfides (pyrite, chalcopyrite, and sphalerite) and anhydrite (Thompson *et al.*, 1988). Major trace elements are as follows (wt %): Co (up to 0.68) in pyrite, Se (up to 0.28) in chalcopyrite, and Ag (up to 0.35) in sphalerite. High Au concentrations (>10 g/t) are only found in bulk samples with dominant sphalerite (Tivey *et al.*, 1995). A high Pt concentration (0.41 g/t) is observed in rare

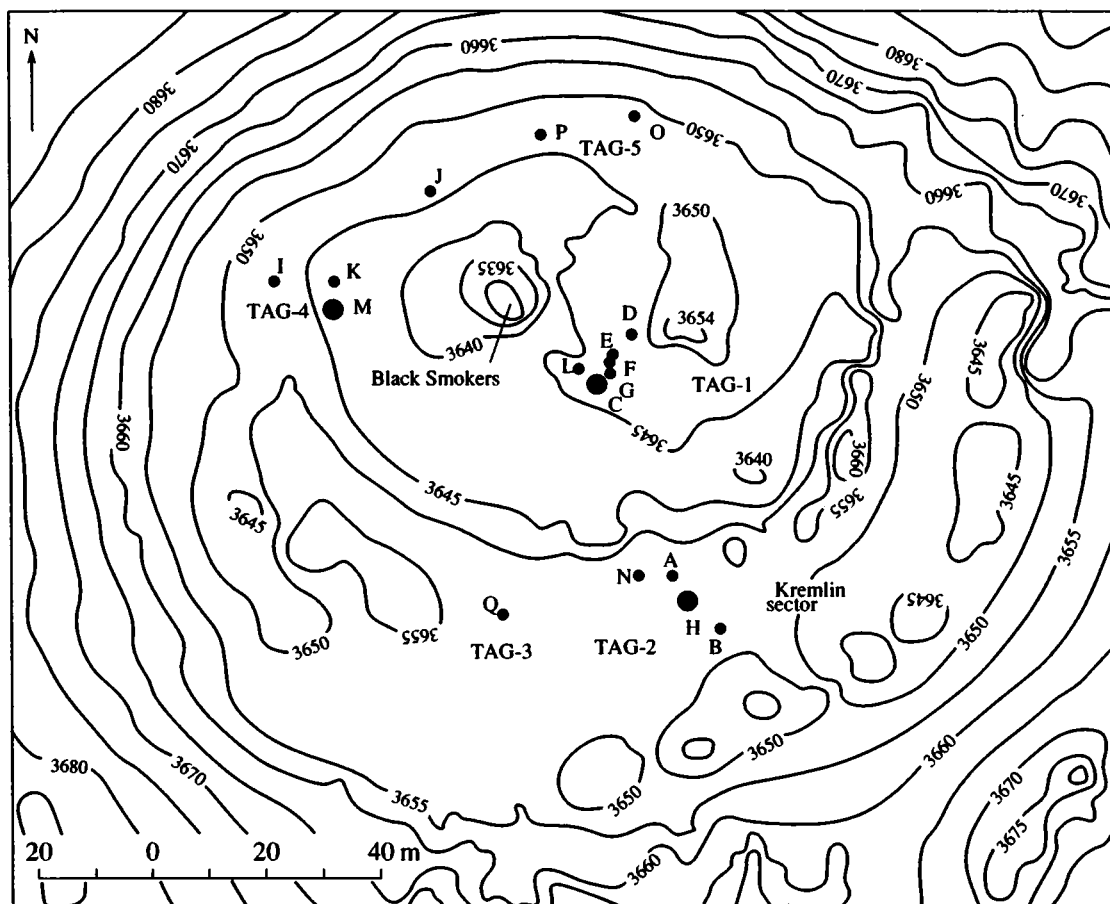


Fig. 2. Location of ODP holes within the active TAG mound, modified after (Knott *et al.*, 1998). Large circles depict sampled holes.

analyses (Krasnov *et al.*, 1995). The analysis of platinum group elements (PGE) in sulfide aggregates revealed that maximal concentrations of Pd (1000 mg/t) are confined to zinc sulfides, while Ir is associated with sulfides of Cu and Fe (Crocket, 1990). The mineralization is characterized by a concentric distribution; the temperature of mineral phases and solutions generally drops from the mound center to the margin (Rona *et al.*, 1986; Tivey *et al.*, 1995).

The data on drilling in 1994 suggest that the deep zone of the mound consists of hydrothermal sulfides of Fe and Cu, along with sulfates and silicates. The mound is underlain by a basaltic stockwork zone. Based on mineralogical and geochemical works (Fouquet *et al.*, 1998; Herzig *et al.*, 1998a; Knott *et al.*, 1995, 1998; and others), ore deposits of this mound are divided into several types replacing each other with depth: hydroxides of Si and Fe, massive pyrite breccia, pyrite-anhydrite breccia, pyrite-anhydrite-quartz breccia, pyrite-quartz breccia, silicified basalt breccia, and chloritized basalt breccia. The top of the pyrite-quartz zone, located at a depth of approximately 38 m, presumably marks the position of ocean floor paleosurface prior to the mound formation (Knott *et al.*, 1998). Relative to the surface

ore, the pyrite-quartz zone is depleted in sphalerite. Pyrite, quartz, anhydrite, and chalcocopyrite comprise more than 90% of the ore material. Sphalerite and marcasite are locally found. Bornite, idaite, digenite, and covellite are minor. Native gold is observed as a rare mineral. Pyrite is ubiquitous in ores, while chalcocopyrite and sphalerite are confined to shallow zones (up to 10–15 m).

The diversity of structures and mineral distribution is manifested at different levels (mound or small samples), and the process of mineral transformation plays a significant role. The near-surface porous sulfides are characterized by spheroidal colloform textures that are preserved as relic forms in deep massive ores as well (Brown and McClay, 1998). Based on the microprobe analysis for trace elements, such as Ag, Se, As, and Co (Knott *et al.*, 1998), only the Co concentration is appreciable in pyrite (<0.04 to 1.96 wt % in 52 analyses out of 128). The analysis of 15 bulk samples and sulfide concentrates from cores revealed that the average concentration of most trace elements, including Au (0.5 g/t), is below the concentration in surface sediments. This phenomenon is attributed to the zonal purification (Herzig *et al.*, 1998a).

MATERIALS AND RESEARCH METHODS

Based on the core description in the preliminary ODP Leg 158 report, we ordered 30 systematically selected samples from holes 957C, 957H, and 957M that represented the three main sectors (TAG 1, TAG 2, and TAG 4). The obtained material characterizes each hole in the depth interval of 0 to 50 m from the present-day mound surface.

The morphology and relationship between minerals were examined on polished sections under an ore microscope and a CamScan scanning electron microscope. The latter was also used to carry out the qualitative determination of composition of some microspecimens. The polished sections were prepared without heating. Grains selected under the microscope were studied with a Camebax SX-50 microprobe under the following laboratory conditions: acceleration 20 kV; beam current 10 nA; count duration 30 s; analytical lines (standards): AuM α , AgL α , PtM α , PdM α , CoK α , SeL α (pure metals), and HgK α (HgTe). Detection limits for elements, calculated according to the formula proposed by Kulikova (1995), are as follows (wt %): Au 0.09, Ag 0.05, Pt 0.08, Pd 0.10, Hg 0.06, Co 0.01, and Se 0.06.

In total, we performed 262 microanalyses of sulfides for noble metals (Au, Ag, Pt, and Pd) and some associated elements (Co, Se, and Hg). We checked Co and Se, since previous researchers had suggested that these elements are abundant in major sulfides from the TAG mound. The examination of Hg was provoked by a complete absence of information concerning this interesting (in terms of genesis) element in the edifice studied. The variable number of analysis for different minerals was dictated by the degree of their abundance. The greatest number of analyses were performed for the dominant pyrite (170 analyses), while the subordinate chalcopyrite was studied by 64 analyses. The rare sphalerite and marcasite were examined by the minimal number of analyses (14 each).

RESULTS OF THE STUDY OF NOBLE METALS AND ASSOCIATED TRACE ELEMENTS IN SULFIDE MINERALS

Based on the generalized analytical results (Tables 1, 2; Fig. 3), the abundance and distribution of trace elements in sulfides are strongly variable. The concentration of all elements, except Pd, is above the detection limit. The maximal concentration of trace elements is as follows (wt %): Co 0.83, Hg 0.38, and Au 0.40. In some cases, Se (0.12 wt %) and Pt (0.13 wt %) are also observed. Hence, the maximal concentration of most elements exceeds 0.1 wt %. However, independent mineral phases of these elements are not detected even under the maximal magnification. The Ag concentration does not exceed 0.09 wt %; however, some of the obtained values are significant, since the detection limit for this element is 0.05 wt %. It is worth noting that all

of the trace element concentrations are characterized by an extremely sporadic distribution; elevated and zero concentrations can be registered in adjacent points within a single grain.

We can judge the degree of element dispersion, based on differences in the distribution of significant (above the detection limit) and trace concentrations of various elements (Table 1; Fig. 3). Among noble metals, significant values of Au are most abundant (in 65 analyses; $n = 262$). The abundance of Ag and Pt is subordinate (46 and 21 analyses, respectively). However, if trace concentrations are also included, the occurrence frequency of Ag (216 analyses) and Pt (147 analyses) is higher, relative to Au (140 analyses). The distribution of Pd traces (132 analyses) is close to the total occurrence frequency of Au. Hence, relative to Au, other noble metals are present in a more dispersed form, although sulfides are known to be characterized by a high concentration of Ag (up to several percents).

In terms of the occurrence frequency of significant concentrations, associated trace elements are arranged in the following order: Co (202 analyses), Hg (132), and Se (49). It should be noted that both Co and Hg are strongly governed by significant values, although Co is only encountered as significant concentrations, while Hg can be present as traces as well. Se is mainly present as traces.

Pyrite is the main carrier of "invisible" Au (significant Au concentrations were registered in 51 analyses; $n = 170$). It is less abundant in chalcopyrite (12 analyses; $n = 64$) and marcasite (2 analyses; $n = 14$). Sphalerite is completely devoid of Au. Silver is abundant in iron disulfides and less common in chalcopyrite. In sphalerite, the occurrence frequency of significant Ag concentrations is minor, but it can increase by one order of magnitude, if trace values are also taken into account. At the same time, sphalerite represents the main carrier of PGE. For example, Pt is found in 2 analyses (or 10 analyses including trace contents; $n = 14$) while Pd traces are found in 8 analyses. A similar occurrence frequency is recorded for Pt in chalcopyrite. The significant Pt concentration is observed in 8 analyses (or 46 analyses including trace values; $n = 64$). The Pt occurrence in iron disulfides is much less frequent.

The confinement of associated trace elements to various sulfides reveals a certain similarity with noble metals. For example, the sulfide sequence based on a decreasing occurrence frequency of Hg is similar to the Au-related version (pyrite–chalcopyrite–marcasite), except for the fact that Hg is occasionally found in the Au-free sphalerite as well (Table 1; Fig. 3). The distribution pattern is similar in the Co–Ag and Se–Pt pairs. Cobalt is abundant in iron disulfides, subordinate in chalcopyrite, and rare in sphalerite. Selenium, which is more common in chalcopyrite than in iron disulfides, is rare in sphalerite, relative to Pt.

When passing from the peripheral Hole 957H (the Kremlin sector with white smokers) to holes 957C and

Table 1. Concentrations (wt %) and occurrence frequency (%) of noble metals and associated trace elements in drill core sulfides from the active TAG mound

Element*		Au (0.09)			Ag (0.05)			Pt (0.08)			Pd** (0.10)		
mineral	N	interval	n_{sig} , k %	n_{tot} , K %	interval	n_{sig} , k %	n_{tot} , K %	interval	n_{sig} , k %	n_{tot} , K %	interval	n_{sig} , k %	n_{tot} , K %
Based on all minerals	262	0.09–0.40	65 24.8%	140 53.4%	0.05–0.09	46 17.6%	216 82.4%	0.08–0.13	21 8%	147 56.1%	<0.10	–	132 52.2%
Pyrite	170	0.09–0.40	51 30%	108 63.5%	0.05–0.09	32 18.8%	142 83.5%	0.08–0.11	10 5.9%	85 50%	<0.10	–	85 51.8%
Chalcopyrite	64	0.09–0.29	12 18.8%	23 35.9%	0.05–0.08	9 14.1%	51 79.7%	0.08–0.13	8 12.5%	46 71.9%	<0.10	–	32 52.5%
Marcasite	14	0.09–0.24	2 14.3%	9 64.3%	0.06–0.07	4 28.6%	13 92.9%	0.08	1 7.1%	6 42.9%	<0.10	–	7 50%
Sphalerite	14	–	–	–	0.05	1 7.1%	10 71.4%	0.08–0.12	2 14.3%	10 71.4%	<0.10	–	8 57.1%

Element*		Hg (0.06)			Co (0.01)			Se (0.06)		
mineral	N	interval	n_{sig} , k %	n_{tot} , K %	interval	n_{sig} , k %	n_{tot} , K %	interval	n_{sig} , k %	n_{tot} , K %
Based on all minerals	262	0.06–0.38	132 50.4%	162 61.8%	0.01–0.83	202 77.1%	–	0.06–0.12	49 18.7%	203 77.5%
Pyrite	170	0.06–0.34	94 55.3%	115 67.6%	0.01–0.83	148 87.1%	–	0.06–0.12	31 18.2%	140 82.4%
Chalcopyrite	64	0.06–0.32	28 43.8%	32 50%	0.01–0.05	38 57.8%	–	0.06–0.08	18 28.1%	44 68.8%
Marcasite	14	0.06–0.38	6 42.9%	10 71.4%	0.01–0.06	10 71.4%	–	<0.06	–	10 71.4%
Sphalerite	14	0.06–0.30	4 28.6%	5 35.7%	0.01–0.04	7 50%	–	<0.06	–	9 64.3%

* Detection limits of elements are given in parentheses; dashes denote intervals of significant element concentration; (**) $n = 253$, including 164 analyses of pyrite and 61 analyses of chalcopyrite; (N) total number of analyses; (n_{sig}) number of analyses with significant element concentration; (k%) detection percentage of significant element concentration in samples analyzed; (n_{tot}) total number of analyses with the specific element; (K%) percentage of analyses with the specific element, including trace values; (–) absence of element or respective data.

957M, which are located nearer to active black smokers, one can observe certain regularities in the occurrence frequency of significant values and maximal concentrations of trace elements in the minerals studied.

Pyrite and chalcopyrite, which have been most analyzed, are highly representative in this respect (Table 2; Fig. 4). In pyrite, the maximal occurrence frequency (43.2%) and concentration of Au (0.40 wt %) are registered in Hole 957H. These values are equal to 25.8% and 0.27 wt %, respectively, for Hole 957C and 25% and up to 0.33 wt %, respectively, for Hole 957M. The total occurrence frequency (including traces) is less variable. Hence, pyrite from central holes contains a higher amount of dispersed Au. In contrast, these parameters for chalcopyrite decrease in central holes. For example, the occurrence frequency and maximal concentration of Au in chalcopyrite are as follows: 7.7% and 0.15 wt % in Hole 957H; 12.5% and 0.18 wt % in Hole 957M; and 25.7% and 0.35 wt % in 957 C (the occurrence frequency including trace concentrations increases as well). Hence, the occurrence frequency of

Au in chalcopyrite is higher in Hole 957C, as compared to other holes (the occurrence frequency is approximately similar but the concentration is higher, relative to the values for pyrite). Thus, chalcopyrite turns out to be the carrier of maximal amounts of Au near the active fluid discharge zone, where the occurrence frequency of Au in chalcopyrite is three times higher, relative to the mound periphery.

A somewhat different trend is revealed with respect to the occurrence of significant concentrations of Ag and Pt in these minerals; the occurrence frequency is minimum for pyrite and chalcopyrite from Hole 957H and maximum for samples from central holes 957M and 957C. At the same time, the Pt distribution is always higher in chalcopyrite, relative to pyrite.

In pyrite, the Co and Se distribution is similar. In central holes 957C and 957M, they are more frequent and abundant than in Hole 957H. The occurrence frequency of these elements in chalcopyrite is reversed; i.e., it is maximum in Hole 957H and appreciably lesser in holes 957C and 957M. The Hg occurrence is similar

Table 2. Comparison of concentrations (wt %) and occurrence frequency (%) of noble metals and associated trace elements in sulfides from various holes on the active TAG mound

Element		Au (0.09)			Ag (0.05)			Pt (0.08)			Pd *(0.10)		
mineral	N	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %
Hole 957M													
Based on all minerals	99	0.09–0.33	18 18.2%	46 46.5%	0.05–0.09	23 23.2%	84 84.8%	0.08–0.10	8 8.1%	53 53.5%	<0.10	–	57 57.6%
Pyrite	60	0.09–0.33	15 25%	33 55%	0.05–0.09	14 23.3%	51 85%	0.08	3 5%	31 51.7%	<0.10	–	37 61.7%
Chalcopyrite	16	0.09–0.18	2 12.5%	5 31.2%	0.05–0.06	4 25%	14 87.5%	0.08–0.10	3 18.8%	8 50%	<0.10	–	7 43.8%
Marcasite	12	0.24	1 8.3%	8 66.7%	0.05–0.07	4 33.3%	11 91.7%	0.08	1 8.3%	6 50%	<0.10	–	6 50%
Sphalerite	11	–	–	–	0.05	1 72.7%	8	0.08	1 72.7%	8	<0.10	–	7 63.6%
Hole 957C													
Based on all minerals	101*	0.09–0.35	26 25.7%	51 50.5%	0.05–0.08	17 16.8%	81 80.2%	0.08–0.11	10 9.9%	47 46.5%	<0.10	–	45 48.9%
Pyrite	66	0.09–0.27	17 25.8%	34 51.5%	0.05–0.08	13 19.7%	53 80.3%	0.08–0.11	6 9.1%	27 40.1%	<0.10	–	29 48.3%
Chalcopyrite	35	0.09–0.35	9 25.7%	17 48.6%	0.05–0.08	4 11.4%	28 80%	0.08–0.10	4 11.4%	20 57.1%	<0.10	–	16 50%
Hole 957H													
Based on all minerals	62	0.09–0.40	21 33.9%	28 45.2%	0.05–0.06	6 9.7%	51 82.3%	0.09–0.13	3 4.8%	37 59.7%	<0.10	–	30 48.4%
Pyrite	44	0.09–0.40	19 43.2%	26 59.1%	0.05–0.06	5 11.4%	37 84.1%	0.09	1 2.3%	27 61.4%	<0.10	–	19 43.2%
Chalcopyrite	13	0.15	1 7.7%	1 7.7%	0.05	1 7.7%	10 77%	0.13	1 7.7%	8 61.5%	<0.10	–	9 69.2%
Marcasite	2	0.09	1	1	<0.05	–	2	–	–	–	<0.10	–	1
Sphalerite	3	–	–	–	<0.05	–	2	0.12	1	2	<0.10	–	1
Element		Hg (0.06)			Co (0.01)			Se (0.06)					
mineral	N	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %	interval	<i>n</i> _{sig} , <i>k</i> %	<i>n</i> _{tot} , K %			
Hole 957M													
Based on all minerals	99	0.06–0.34	50 50.5%	65 65.7%	0.01–0.83	78 78.8%	–	0.06–0.12	12 12.1%	72 72.7%			
Pyrite	60	0.06–0.34	36 60%	44 73.3%	0.01–0.83	55 91.7%	–	0.06–0.12	10 16.7%	47 78.3%			
Chalcopyrite	16	0.07–0.28	7 43.8%	9 56.2%	0.01–0.03	9 56.2%	–	0.08	2 12.5%	9 56.2%			
Marcasite	12	0.06–0.14	4 33.3%	8 66.7%	0.01–0.06	8 66.7%	–	<0.06	–	9 75%			
Sphalerite	11	0.18–0.30	3 27.3%	4 36.4%	0.01–0.04	6 54.5%	–	<0.06	–	7 63.6%			
Hole 957C													
Based on all minerals	101*	0.06–0.28	31 30.7%	48 47.5%	0.01–0.38	82 81.2%	–	0.06–0.09	16 15.8%	77 76.2%			
Pyrite	66	0.06–0.28	23 34.8%	35 53%	0.01–0.38	56 84.8%	–	0.06–0.09	13 19.7%	52 78.8%			

Table 2. (Contd.)

Element		Hg (0.06)			Co (0.01)			Se (0.06)		
mineral	N	interval	$n_{\text{sig}}, k \%$	$n_{\text{tot}}, K \%$	interval	$n_{\text{sig}}, k \%$	$n_{\text{tot}}, K \%$	interval	$n_{\text{sig}}, k \%$	$n_{\text{tot}}, K \%$
Chalcopyrite	35	0.06–0.20	8 22.9%	13 37.1%	0.01–0.06	26 74.3%	–	0.06–0.09	3 8.6%	25 71.4%
Hole 957H										
Based on all minerals	62	0.06–0.38	28 45.2%	30 48.4%	0.01–0.70	50 80.6%	–	0.06–0.08	8 12.9%	54 87.1%
Pyrite	44	0.06–0.33	21 47.8%	22 50%	0.01–0.70	36 81.8%	–	0.06–0.08	6 13.6%	40 90.9%
Chalcopyrite	13	0.12–0.32	4 30.8%	5 38.5%	0.01–0.04	11 84.6%	–	0.01–0.07	2 15.4%	11 84.6%
Marcasite	2	0.10–0.38	2	2	0.02–0.05	2	–	<0.06	–	1
Sphalerite	3	0.23	1	1	0.01	1	–	<0.06	–	2

* $n = 92$, including 60 analyses of pyrite and 32 analyses of chalcopyrite. Other legends as in Table 1.

for pyrite and chalcopyrite. This element is most common in Hole 957M and rare in Hole 957C. The occurrence frequency and maximal concentration of Hg in pyrite are always higher than in chalcopyrite (Table 2).

Based on pyrite, which represents the major mineral and main carrier of most elements studied, one can see that concentrations of noble metals in this mineral are stable with respect to depth in different holes. Elevated concentrations (>0.1 wt % Au, 0.5 wt % Ag, and 0.8 wt % Pt) are observed at both upper and lower levels (Fig. 5). The Hg distribution exhibits a similar pat-

tern. Only Co displays an insignificant normal correlation between maximal concentration and depth in holes 957C and 957H.

Thus, the obtained results suggest certain regularities in the distribution of noble metals in the zone extending from white smokers to black smokers. When passing from the periphery (Hole 957H) to the mound center (holes 957C and 957M), one can observe that maximal concentrations and occurrence frequency of Au are increased in chalcopyrite but decreased in

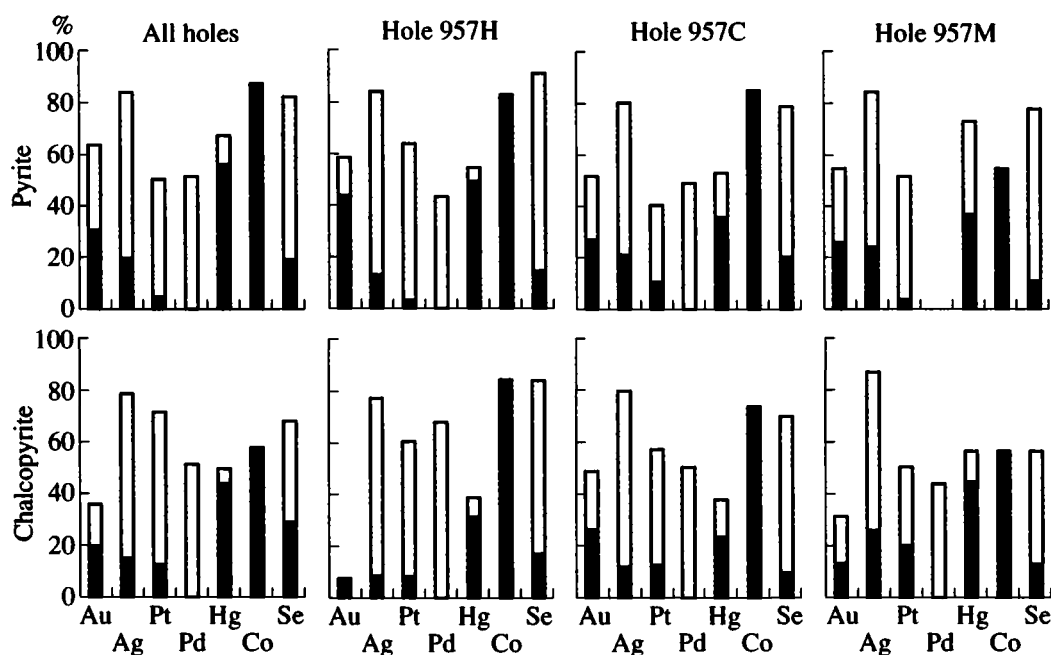


Fig. 3. Occurrence frequency histograms of trace elements in core samples from the active TAG mound. For legend see Fig. 4.

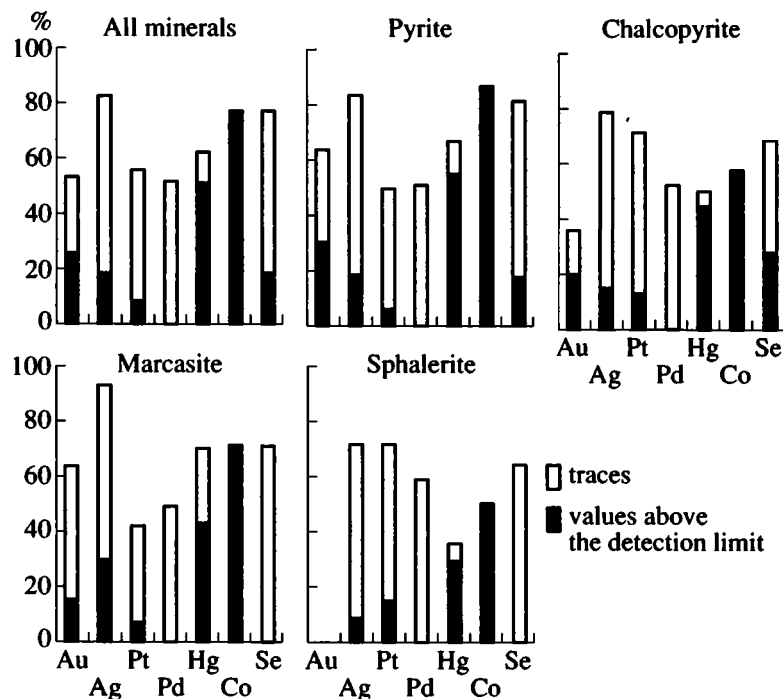


Fig. 4. Occurrence frequency histograms of trace elements in pyrite and chalcopyrite from different holes.

pyrite. In the case of Pt and Ag, these parameters are elevated in both chalcopyrite and pyrite.

STRUCTURAL RELATIONSHIPS BETWEEN MINERALS AND DISTRIBUTION OF NOBLE ELEMENTS IN HETEROGENEOUS CRYSTALS AND AGGREGATES

Despite a simple mineral composition of ores, structural relationships between sulfides in core samples from the TAG mound are highly intricate and diverse (Knott *et al.*, 1998).

Sulfides in cavities make up crystal aggregates with simple relationships, testifying to a sequential accretion of different minerals and a possible combined growth of some species (Figs. 6a–6e). At the same time, transverse sections of cubic pyrite crystals (Fig. 6f) reveal an intricate evolution; the rounded colloform pyrite is enclosed in pentagondodecahedral crystals, which are, in turn, enclosed in cubic crystals. Thus, colloform pyrite represents the earliest generation that subsequently underwent diverse transformations. This is obviously the primary factor responsible for the abundance of sphere- and oval-shaped segregations with a concentric-zonal structure of aggregates in samples from different holes and depths. The mineral phase correlation and trace element distribution in such aggregates are extremely diverse. This is clearly seen in polished sections presented in this work. It should be noted that the brightness of minerals in reflected electron images is naturally different from the ore microscope

version. In our work, analytical data characterize the maximal trace element concentrations in grains, and trace concentrations (i.e., concentrations below the detection limit) are not indicated.

As is evident from Fig. 7, the concentric-zonal pattern is related to concentric zones of chalcopyrite (often with quartz) or sphalerite in pyrite, as well as pyrite zones with a variable degree of crystallization. The sulfide is commonly distributed along boundaries between coarse-crystalline pyrite of the core and fine-crystalline pyrite of the rim. Chalcopyrite is observed as an irregular dissemination in the pyrite core or as a substance emphasizing the internal concentric structure of aggregates (Fig. 7d). The coarse-crystalline pyrite core is often surrounded by rims composed of fine pyrite and chalcopyrite (Figs. 7e, 7f). The abundance and distribution of trace elements in such aggregates are variable. For example, Au is absent in all phases of the concentric-zonal pyrite–chalcopyrite aggregate in samples from Hole 957H (depth 8.7 m). As is evident from the trace element distribution in Fig. 7a (wt %), the Se concentration in chalcopyrite (0.07) is higher than in the dominant pyrite (traces), while both chalcopyrite and pyrite contain similar amounts of Co (0.03 and 0.02, respectively) and Hg (0.19 and 0.15, respectively). The Au concentration is increased in the rosette-shaped core of coarse-crystalline pyrite (Fig. 7b) and decreased in the outer fine-crystalline zone. It is absent in the chalcopyrite patch. At the same time, Se is abundant in the pyrite fringe and chalcopyrite. The trace element composition of minerals is given below (wt %): coarse-

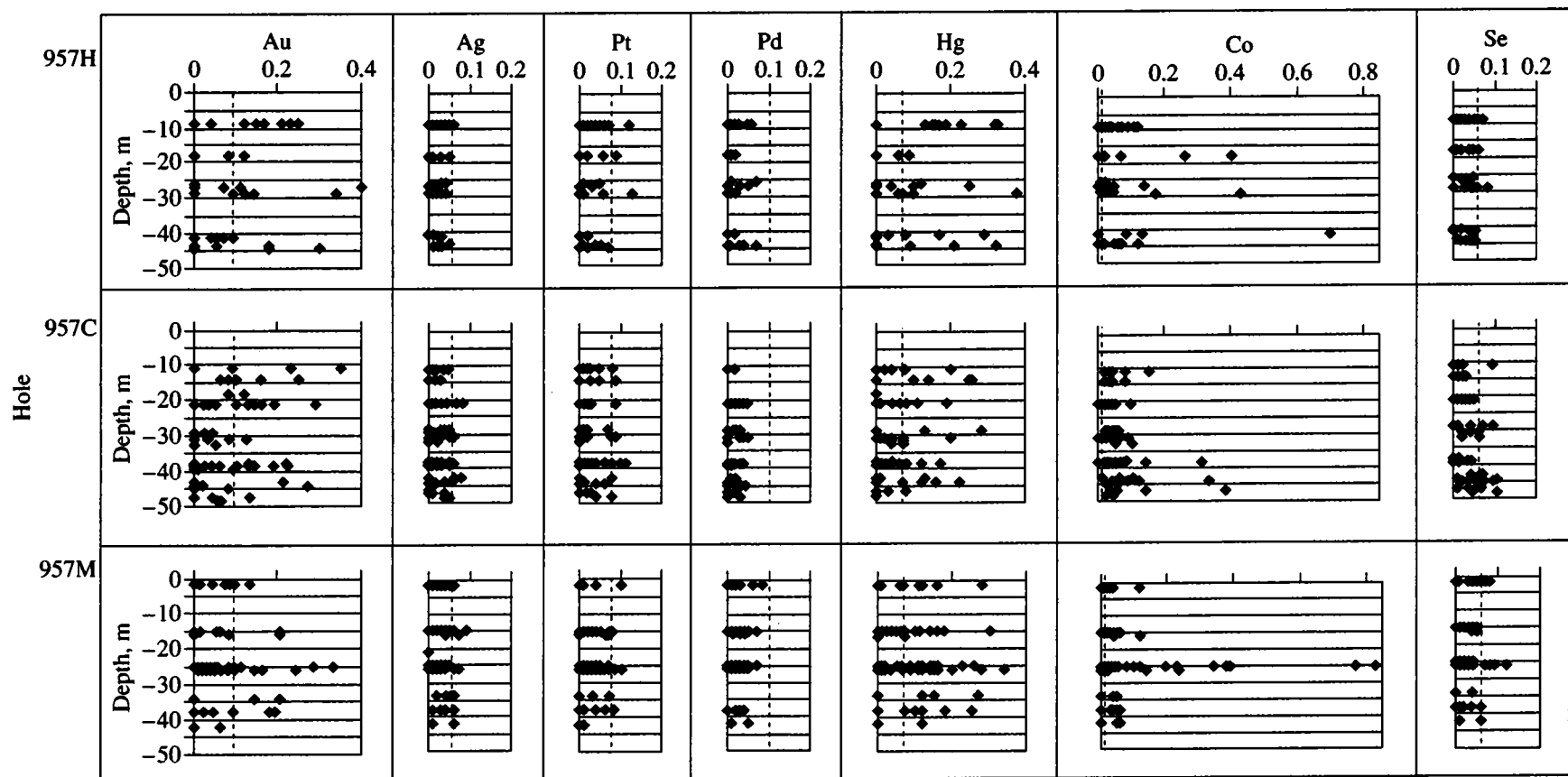


Fig. 5. Variation of trace element concentration intervals (wt %) in pyrite vs. depth in different holes (dash-and-dot lines designate detection limits of elements).

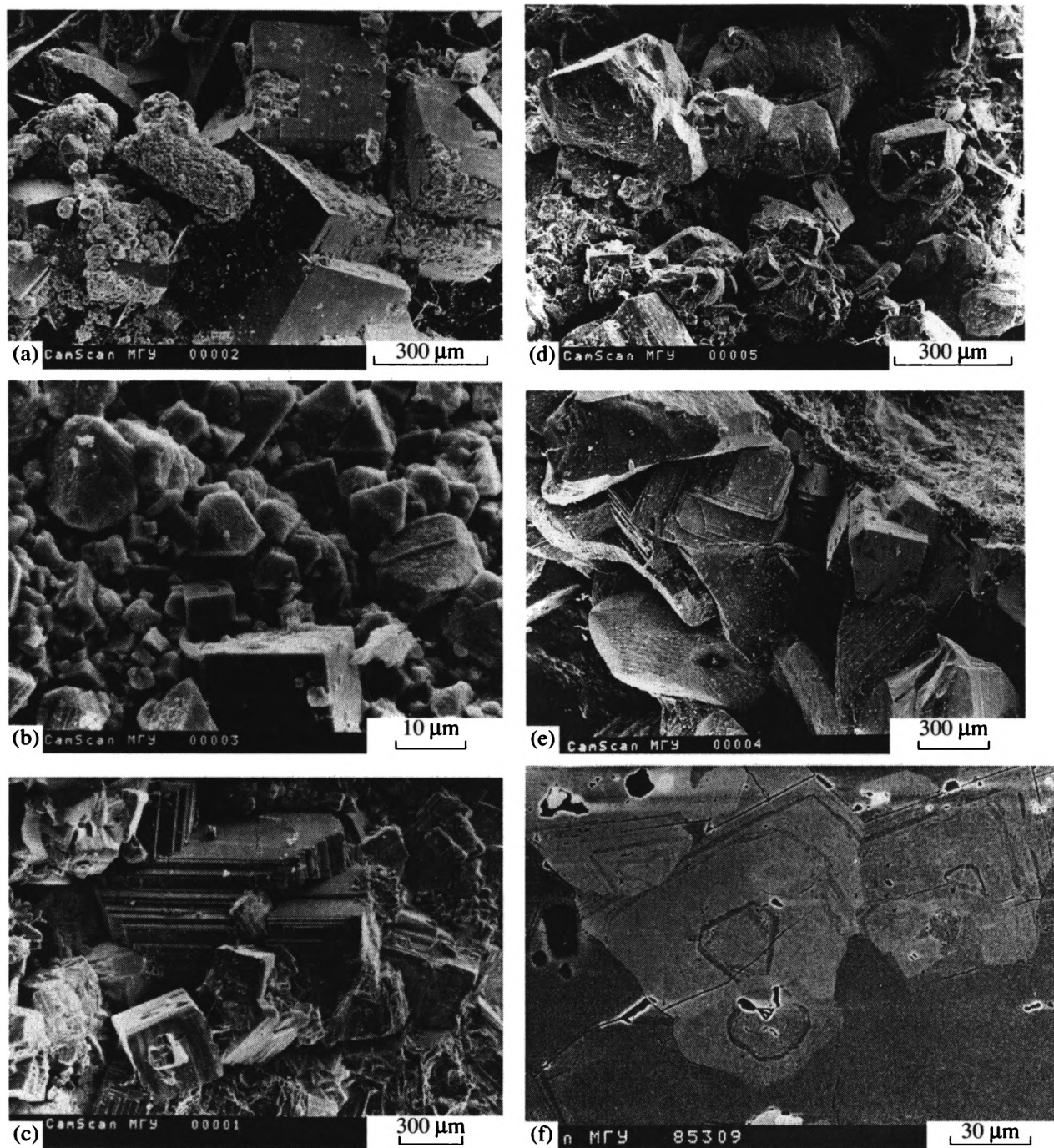


Fig. 6. Sulfide crystals from different holes on the TAG mound. Reflected electron images. (a) Sample M-5R-1.p.8 (depth 25 m), aggregate of cubic pyrite crystals with crusts and solitary fine crystals of sphalerite; (b) another sector of the same sample, accretion of cubic pyrite and tetrahedral sphalerite crystals; (c) sample C-10N-1.p.3 (depth 29 m), accretion of cubic pyrite crystals with striation (a microdruse of fine quartz crystals on pyrite is seen on the left side); (d) sample C-7N-2.p.1D (depth 22 m), aggregate of chalcopyrite crystals and smaller (cubic) pyrite crystals; (e) sample H-9x-1.p.4 (depth 45 m), aggregate of chalcopyrite crystals; (f) sample M-5R-1.p.15 (depth 26 m), polished section, evolution of pyrite growth (primary, rounded colloform segregations are enclosed in pentagondodecahedral (?) crystals subsequently overgrown with cubic crystals).

grained pyrite—Au up to 0.17, Hg 0.15, and Co 0.02; fine-grained pyrite—Au 0.12, Se 0.06, and Co 0.01; and chalcopyrite—Co 0.04 and Se 0.06. In the adjacent sector with fine chalcopyrite inclusions in sphalerite

(Fig. 7c), Au is restricted to chalcopyrite, while Pt and Ag are associated with sphalerite and pyrite, respectively. In sphalerite and chalcopyrite, the Hg concentration is similar and exceeds the value for pyrite. The

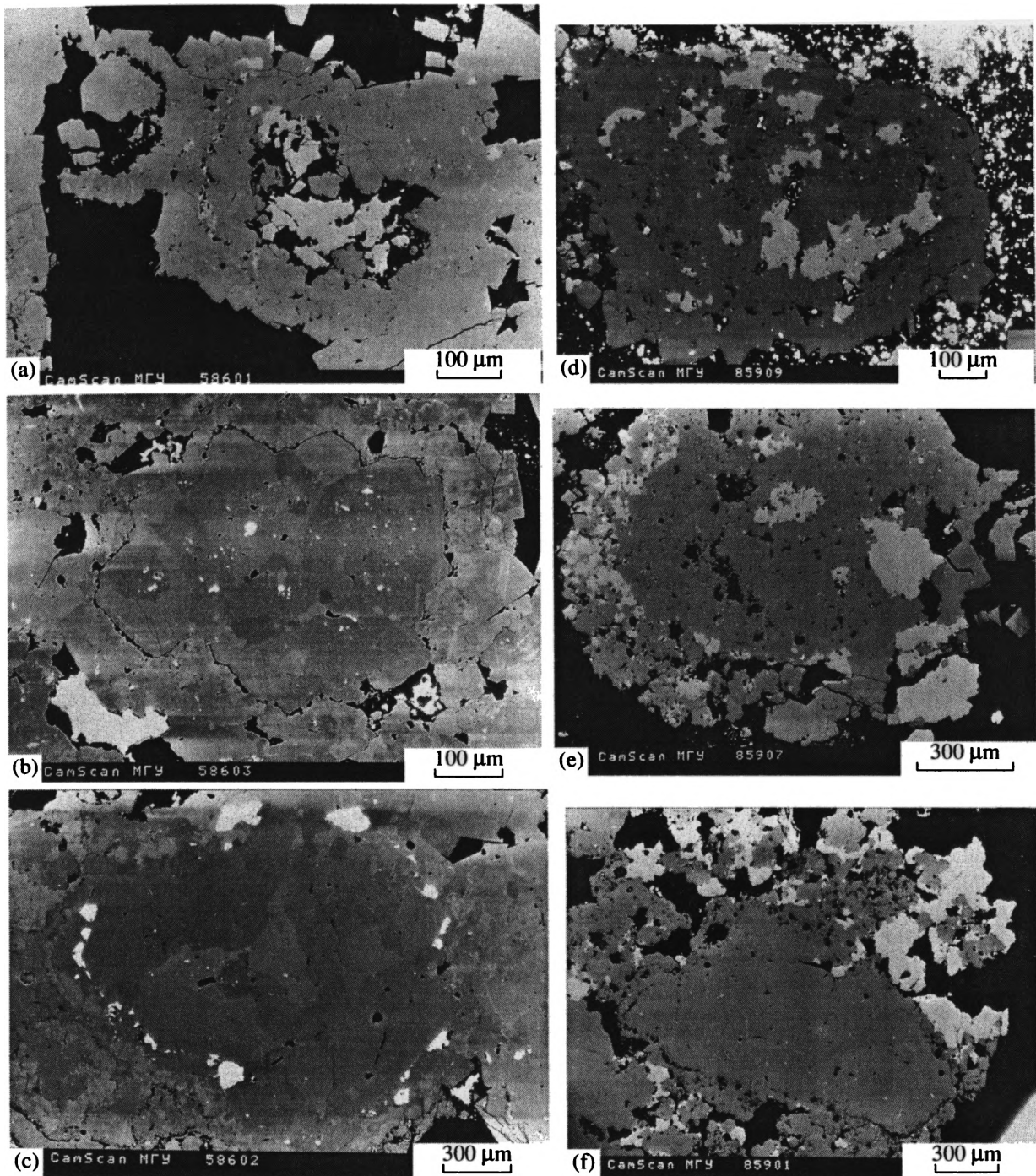


Fig. 7. Concentric-zonal aggregates in holes 957H and 957C. Polished sections, reflected electron images. Sample H-1N-1.p.2 (depth 8.7 m): (a) concentric-zonal aggregate of chalcopyrite (white), pyrite (gray shades), and quartz (black), (b) rosette-shaped pyrite with a fine-crystalline pyrite rim, white small inclusions and patches of chalcopyrite (below), (c) concentric-zonal pyrite with a fine-crystalline rim (the contact zone is marked with fine sphalerite crystals, tiny chalcopyrite inclusions are observed beyond the image field, and the matrix is composed of nodular pyrite); (d) sample C-4W-1.p.2 (depth 11 m), concentric-zonal pyrite with chalcopyrite (pale gray) outlining the aggregate structure (white fine grains in the image periphery are related to the Ag paste); (e) sample H-1N-1.p.9D (depth 9 m), oval pyrite (gray) with chalcopyrite dissemination (white) and a rim of fine pyrite and chalcopyrite grains; (f) sample C-7N-2.p. 1D (depth 21 m), zonal aggregate with a central pyrite core and recrystallized outer zone of fine pyrite and coarser chalcopyrite.

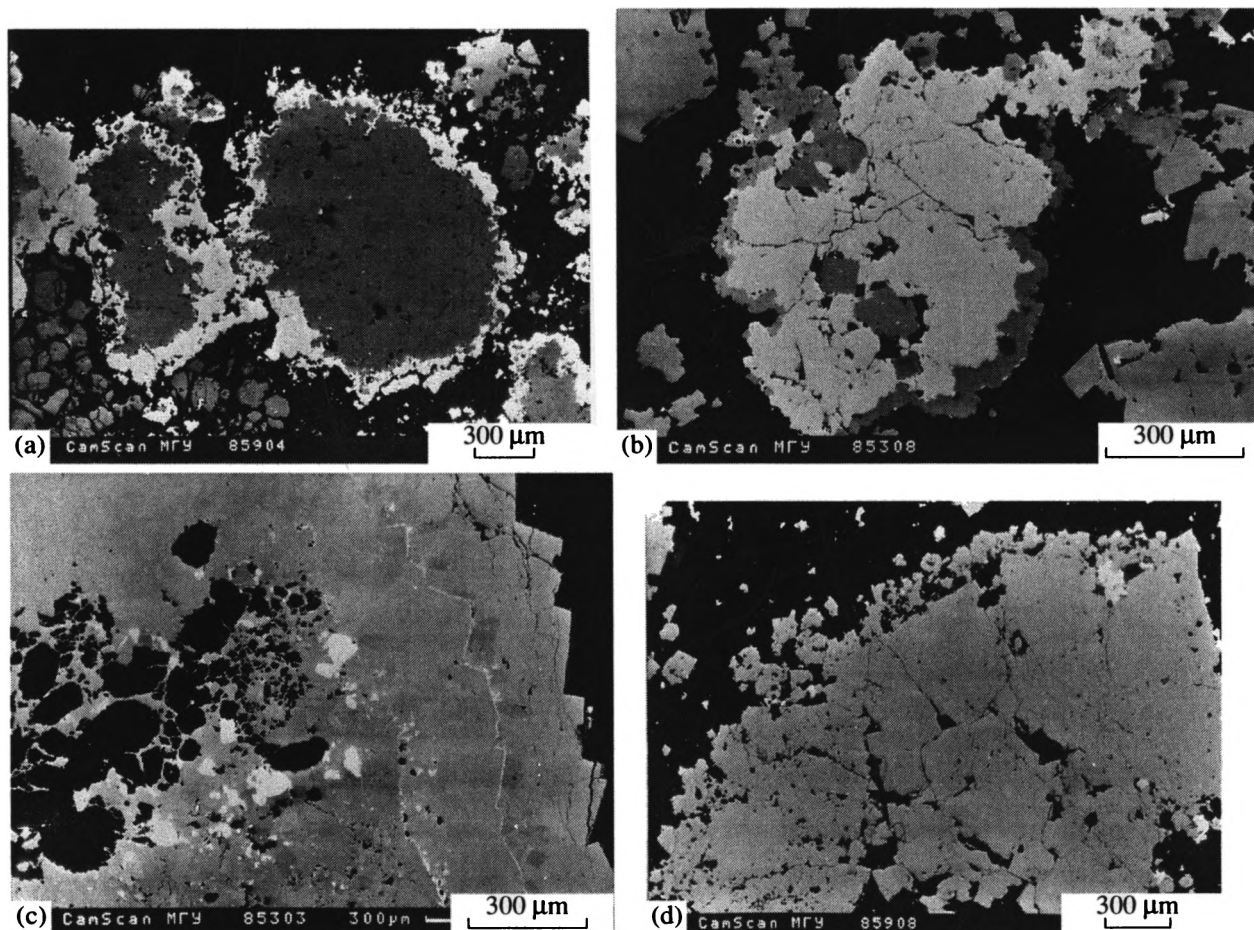


Fig. 8. Concentric-zonal mineral aggregates from different depths of Hole 957M. Polished sections, reflected electron images. (a) Sample M-SR-1.p.1 (depth 38 m), quartz (black) and pyrite patch (gray) surrounded by chalcopyrite (white); (b) sample M-SR-1.p.15 (depth 26 m), quartz (black) and chalcopyrite patch (white) with pyrite fringe and euhedral pyrite inclusions (gray); (c) sample M-3R-1.p.12 (depth 15 m), quartz (black), sphalerite (white) in zonal pyrite, along with the contact zone marked by thin bands of sphalerite and marcasite (darker than pyrite); (d) sample M-1R-2.p.6 (depth 1.6 m), coarse-crystalline pyrite (gray) and fine-crystalline pyrite rim with rare chalcopyrite inclusions (white).

trace element composition of minerals is as follows (wt %): coarse-crystalline pyrite—Hg 0.10, Co 0.03, and Ag 0.05; sphalerite—Pt 0.12 and Hg 0.23; chalcopyrite—Au 0.15, Hg 0.23, and Co 0.02. In an analogous sample from Hole 957C (depth 11 m), Au in chalcopyrite is associated with a high Hg content, and the Co content is lower than in the ambient pyrite (Fig. 7d). The pyrite includes Co (0.15 wt %), while the chalcopyrite contains Au (0.35), Hg (0.20), and Co (0.04).

In outer zones, concentric aggregates of fine pyrite crystals and chalcopyrite are characterized by an inverse trend in the trace element distribution between minerals. In such aggregates from Hole 957H (depth 9 m), Au is confined to pyrite fringes and associated with significant Ag, Hg, and Co (Fig. 7e). This conclusion is based on the trace element composition of minerals (wt %): fine-grained pyrite in the fringe—Au 0.25, Ag 0.06, Hg 0.33, and Co up to 0.11; central pyrite grain—Hg 0.16 and Co 0.09; chalcopyrite dis-

semination within the central pyrite grain—Hg 0.32 and Co 0.03; and fine-grained chalcopyrite in the fringe—traces of Ag and Se. In an analogous aggregate from Borehole 957C (depth 21 m), the trace element composition is as follows (%): chalcopyrite in the outer zone—Au 0.29; pyrite in the fringe—Au 0.14, Pt 0.09, and Hg 0.19; pyrite in the core—Au traces, Ag 0.07, and Co 0.10. Hence, the Au concentration is maximal in chalcopyrite but low in pyrite from the fringe and negligible in pyrite from the core (Fig. 7f).

Analogous rounded, concentric-zonal aggregates with various fringes and trace element distribution styles are also observed in Hole 957M (Fig. 8). In the sample from a depth of 38 m (Fig. 8a), the oval-shaped pyrite aggregate and the chalcopyrite fringe have similar concentrations of Au, Ag, Pt, and Co; however, the pyrite is characterized by higher concentrations of Hg. The trace element composition of minerals is as follows (wt %): pyrite—Au 0.19, Ag 0.06, Pt 0.08, Hg 0.25, and

Co 0.04; chalcopyrite—Au 0.18, Ag 0.06, Pt 0.08, Hg 0.18, and Co 0.03. In the sample from a depth of 26 m (Fig. 8b), euhedral pyrite crystals within an oval chalcopyrite patch contain Au, which is absent in the chalcopyrite proper and pyrite rim. The trace element composition of minerals is as follows (wt %): pyrite dissemination—Au 0.16 and Co 0.03; pyrite fringe—Co 0.01; and chalcopyrite—Co 0.03. The polymineral concentric-zonal aggregate from a depth of 15 m (Fig. 8c) is composed of banded-zonal pyrite with quartz and sphalerite in the center and thin bands of sphalerite and marcasite along zone boundaries. Here, Au is only registered in the outermost zone with euhedral boundaries, while Pt is observed in the Au-free sphalerite and marcasite. The Hg concentration is maximal in sphalerite but almost similar in pyrite and marcasite, as is evident from the trace element composition (wt %): pyrite in the outer zone—Au 0.14, Hg 0.16, and Co 0.06; marcasite—Pt 0.08, Hg 0.14, and Co 0.02; and sphalerite—Pt 0.08, Hg 0.30, and Co 0.02. At a depth of 1.6 m (Fig. 8d), the coarse-crystalline pyrite is surrounded by fine, partially euhedral pyrite crystals. The trace element composition is as follows (wt %): coarse-crystalline pyrite—Hg 0.12 and Co 0.04; pyrite in the fringe—Au 0.13, Pt 0.10, Hg 0.16, Co 0.03, and Se 0.08; and chalcopyrite—Hg 0.16 and Co 0.03. Thus, pyrite grains in the central zone are characterized by elevated Hg concentrations, while fine crystals in the fringe have high concentrations of Au, Pt, and Hg. The Co content is approximately similar. The chalcopyrite is Au-free.

The examples described above suggest the following conclusions. In samples from deep zones of Hole 957M, Au is mainly concentrated in coarse-crystalline pyrite grains in the central zone or in chalcopyrite in the outer shell. It is absent in the marginal, fine-crystalline pyrite grains. In near-surface sectors, Au is concentrated in the outer recrystallized zone, where Pt and Ag are also abundant.

The oval-shaped and rounded, banded-zonal, quartz-pyrite aggregates can also be formed as a result of the development of minerals after organic remains. The subsequent recrystallization and segregation of minerals into separate zones were likely accompanied by a redistribution of trace elements. Since our study embraces an approximately 50-m-thick interval, which mainly corresponds to hydrothermal ores formed on an ocean floor surface that was probably located at a depth of about 38 m from the present-day surface, and vent biota is abundant here (Thompson *et al.*, 1988), the replacement of organic remains by sulfides is quite natural.

The relationships described above are also observed in other holes. At a depth of 14 m in Hole 957C, one can see well-preserved pseudomorphoses of quartz-bearing pyrite after organic remains (Fig. 9a). The pyrite contains almost equal Au and Hg concentrations (up to 0.25–0.26 wt %) and negligible Co (up to 0.08 wt %). At a depth of 41 m in Hole 957H (Figs. 9b, 9c), similar

oval-shaped pyrite-quartz aggregates are more recrystallized, but they contain less Au (up to 0.09 wt % in the coarse-crystalline pyrite and 0.05 wt % in the fine-crystalline variety). The Co and Hg concentrations are high (up to 0.70 and 0.29 wt %, respectively). In some images, one can see a banded-zonal distribution of pyrite and quartz (Fig. 9c). It cannot be ruled out that a part of such aggregates were formed during the alteration of basalt.

Recrystallization processes can also result in the origination of concentric-zonal pyrite-quartz aggregates, in which the central, large pyrite grain is successively surrounded by zones of pure quartz and fine pyrite grains (Fig. 9d). Such relationships are mainly observed in the lower section of all holes studied. For example, at a depth of 47 m in Hole 957C (sample C-16 N-1.p.9), the typical intricate contact between pyrite and quartz is caused by a metasomatic growth of quartz crystals toward the pyrite (Figs. 9d, 9e). Like in pseudomorphoses described above, Au is abundant in the central, large pyrite aggregate (0.13 wt %) and is absent in fine grains from the rim. The Co content is almost similar (0.03 and 0.05 wt %, respectively). In the more recrystallized sector, where the ring structure is almost completely replaced, large Au-free pyrite grains are marked by an elevated Co content (up to 0.34 wt %). Quartz metacrystals are formed along pyrite grain boundaries and cracks within pyrite crystals (Fig. 9f).

In addition to concentric-zonal aggregates with the structural heritage of older segregations, we can also observe other relationships between minerals, testifying to various epigenetic transformations of mineral substance during the mound evolution. Some examples are presented in Fig. 10.

At a depth of 44.5 m in Hole 957H, this kind of relationship is distinctly manifested in the pyrite-chalcopyrite aggregate (Fig. 10a), in which the coarse-crystalline pyrite is intensely corroded by chalcopyrite, which, in turn, is overgrown with fine euhedral (cubic) pyrite crystals. A similar relationship is observed in the pyrite-quartz aggregate (Fig. 10b), in which the coarse-crystalline and massive pyrite (Au 0.30–0.18 wt %, Co 0.05–0.06 wt %) is corroded by the fine-crystalline nonmetallic matrix with tiny euhedral pyrite crystals (Co 0.07–0.12 wt %). The lack of Au in tiny pyrite crystals and its high content in the coarse-crystalline variety suggest that euhedral crystals were formed as a result of the redeposition of an excess pyrite left after the replacement by quartz.

The relationships described above demonstrate the zonal evolution of pyrite crystals (Fig. 6f). We can also observe crystals with a central porous zone of contaminated core and an outer zone of pure pyrite (Fig. 10c, Hole 957M, depth 34 m). The core is characterized by high contents of Au (0.20 wt %), Ag (0.05), Pt (0.07), Hg (0.27), and Co (0.04), whereas the outer zone only contains Ag (0.06) and Co (0.05). At a depth of 25 m in the same hole (Fig. 10d), we noted relationships in the

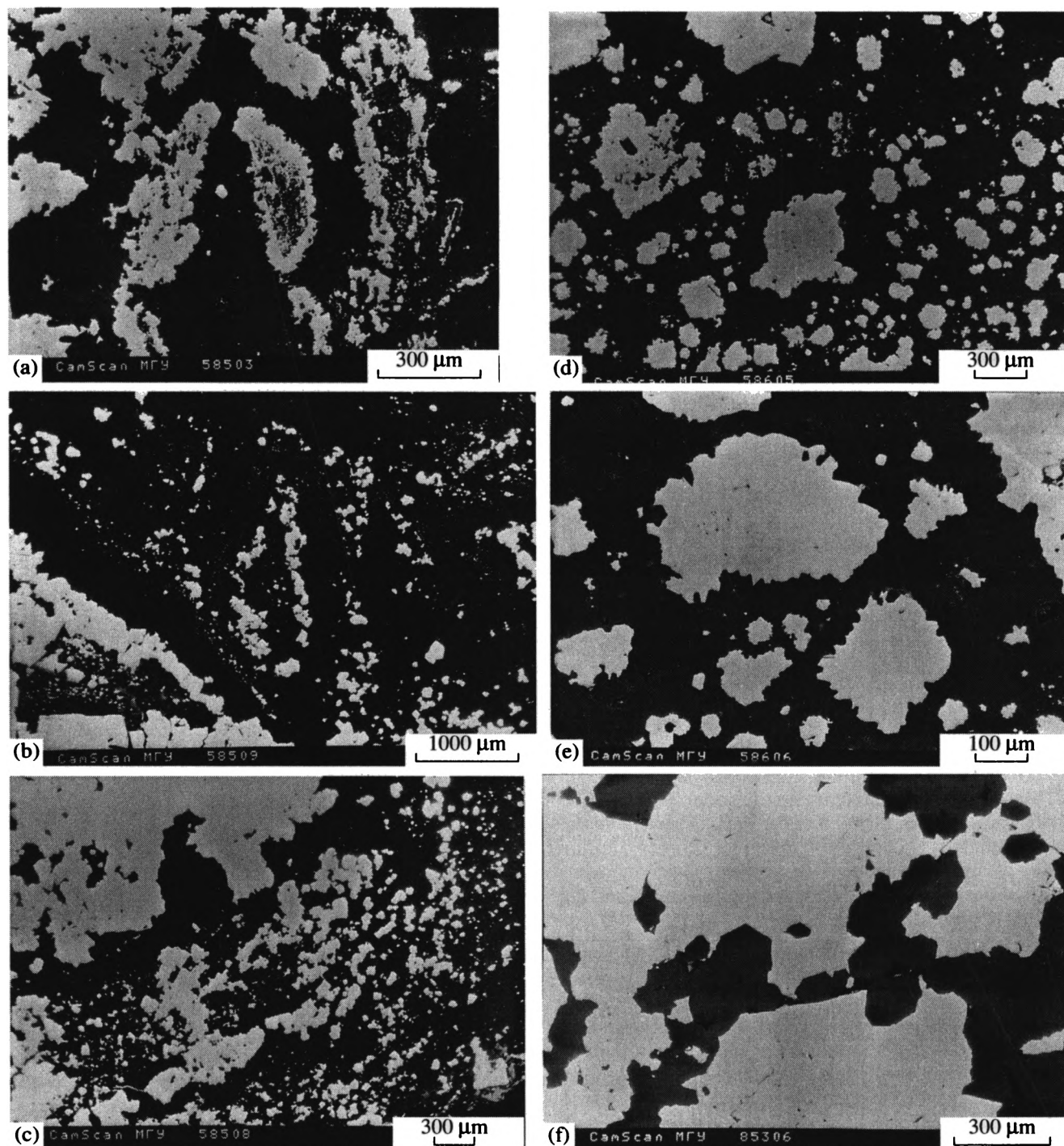


Fig. 9. Pyrite-quartz aggregates. Polished sections, reflected electron images. (a) Sample C-6W-1.p.3 (depth 14 m), pyrite pseudomorphs (white) after organic remains and quartz (black); (b, c) sample H-8N-1.p.9 (depth 41.5 m), recrystallized to variable extent quartz-pyrite pseudomorphs after organic remains; sample C-16N-1.p.9 (depth 47 m): (d) concentric-zonal quartz (black) with a fine-grained pyrite halo (white) around the central pyrite patch, (e) typical intricate contact between pyrite and quartz related to the metasomatic replacement of pyrite by quartz; (f) metasomatic replacement of pyrite by quartz along cracks in a more recrystallized pyrite-quartz aggregate.

pyrite-quartz aggregate suggesting the segregation of pyrite and quartz. The fine-crystalline pyrite-quartz aggregate includes a stringer-type pure quartz with a chain of large pyrite crystals along the center. Relative to the fine-crystalline pyrite, the coarse-crystalline variety is depleted in trace elements, as is evident from their compositions (wt %): fine-crystalline pyrite—Au 0.33, Hg 0.26, and Co 0.83; and coarse-crystalline pyrite—Au 0.11, Hg 0.16, and Co 0.38.

The relationships between minerals are also diverse in breccia ores. Fine pyrite stringers are seen along the boundaries of quartz grains with local swells and rare, fine pyrite metacrystals (Fig. 10e, Hole 957M, depth 15 m). Neogenic, euhedral quartz crystals are also developed on large fragments (upper right-hand corner). The pyrite is Au-free but contains Ag (0.05–0.09 wt %), Hg (0.07–0.16), and Co (0.04–0.06). Inverse relationships are also registered. For example, the fine-clastic pyrite breccia can be enclosed in a non-metallic stringer crosscutting the massive pyrite (Fig. 10f, Hole 957H, depth 41 m). The fine-clastic pyrite contains 0.09 wt % Au, which is missing in the massive variety.

The examples discussed above do not represent an exhaustive record of the entire diversity of structural relationships in the TAG mound. However, they testify to an intense epigenetic transformation of ore aggregates and the subsequent redistribution of trace elements. As mentioned above, the noble metal distribution in minerals generally does not reveal any significant variations with depth (Fig. 3). Nevertheless, summarized analytical data on Au in heterogeneous crystals and aggregates suggest that this metal displays some variation with depth (Table 3). At deep levels of holes studied, crystal and aggregate margins (i.e., outer zones of crystals and concentric-zonal aggregates), recrystallized fringes, ring-shaped haloes around large grains, and so forth are depleted in Au, relative to central zones. In contrast, such formations are enriched in Au in the near-surface level. This trend fits the widely recognized concept of material remobilization during the zonal purification (Hannington *et al.*, 1986; Tivey *et al.*, 1995; and others). According to this concept, Au is released from the lower section of ore bodies as a result of the transformation of minerals under the influence of high-temperature hydrothermal solutions percolating in older rocks. Thus, this metal is redeposited in overlying sectors.

DISCUSSION AND CONCLUSION

Since Au is the most widespread trace element, we shall focus our attention on the behavior of this metal.

Significant Au concentrations, sporadically encountered in sulfides from core samples of the TAG mound, evidently suggest that Au and sulfides were simultaneously delivered and deposited from high-temperature solutions. This conclusion is also supported by elevated

Au concentrations in the central, least altered zones of pyrite crystals and aggregates at lower levels of holes. Based on experimental data (Kozarenko *et al.*, 1986), the joint precipitation of Au and sulfides results in the formation of a metastable Au-bearing iron sulfide, which is subsequently decomposed into pyrite and fine-dispersed Au. The primary Au introduction by high-temperature fluids was discussed earlier with respect to the mound surface (Crocket, 1990). Similar conclusions were derived from the study of Au and Ag in sulfides from the inactive Mir mound (Mozgova *et al.*, 1997, 1998a, 1998b).

We have revealed a heterogeneous distribution of noble metals in sulfides from core samples. This observation fits the model of heterogeneous distribution of Au and Ir in sulfide samples from the mound surface (Crocket, 1990), as well as the high scatter of values of the noble metal concentration in bulk sulfide samples from surface (Tivey *et al.*, 1995) and drill cores (Herzig *et al.*, 1998; Miller, 1998). The extremely heterogeneous distribution of trace elements is known to be evidence of a highly disequilibrium environment, which was predetermined by the vigorous fluid effusion mentioned above. Therefore, calculations based on equilibrium dynamics should be used with great caution in such conditions.

Horizontal and vertical mineralogical-geochemical zonations in the TAG mound are discussed in several works (Herzig *et al.*, 1998; Knott *et al.*, 1998; Tivey *et al.*, 1995; and others). According to these works, when passing from the center (black smokers) to the southeastern flank (the Kremlin sector with white smokers), high-temperature, Cu- and Fe-rich ores are replaced by lower temperature Zn-, Cu-, and Fe-rich ores. In all holes studied, the ore material is enriched in pyrite with increasing depth. Our mineralogical observations in the approximately 50-m-thick interval of holes also indicate that sphalerite and chalcopyrite are primarily concentrated in the near-surface zone.

The Au distribution in sulfides also reveals a zonal pattern. Both on the surface (Tivey *et al.*, 1995) and in deep zones (our data), maximal Au concentrations are confined to the Kremlin sector (Hole 957H). In the mound center (Hole 957C), Au is decreased in pyrite but increased in chalcopyrite. In the chalcopyrite, the Au content is locally higher than in pyrite. Thus, we observe a replacement of the carrier of maximal Au concentrations along the horizontal direction. The vertical distribution of Au is even more dramatic. In bulk sulfide samples from the surface, the Au content ranges between 0.1 and 20.75 g/t (Tivey *et al.*, 1995). In core samples from holes, it varies from <5 mg/t to 3.2 g/t (average 0.5 g/t), according to Herzig *et al.* (1998), or from 0.01 to 2.8 g/t, according to Miller (1998). Hence, the Au concentration is decreased by one order of magnitude in deep zones of the mound. Tables presented in (Tivey *et al.*, 1995) show that maximal Au concentrations (>10 g/t) are inherent to sphalerite-dominated

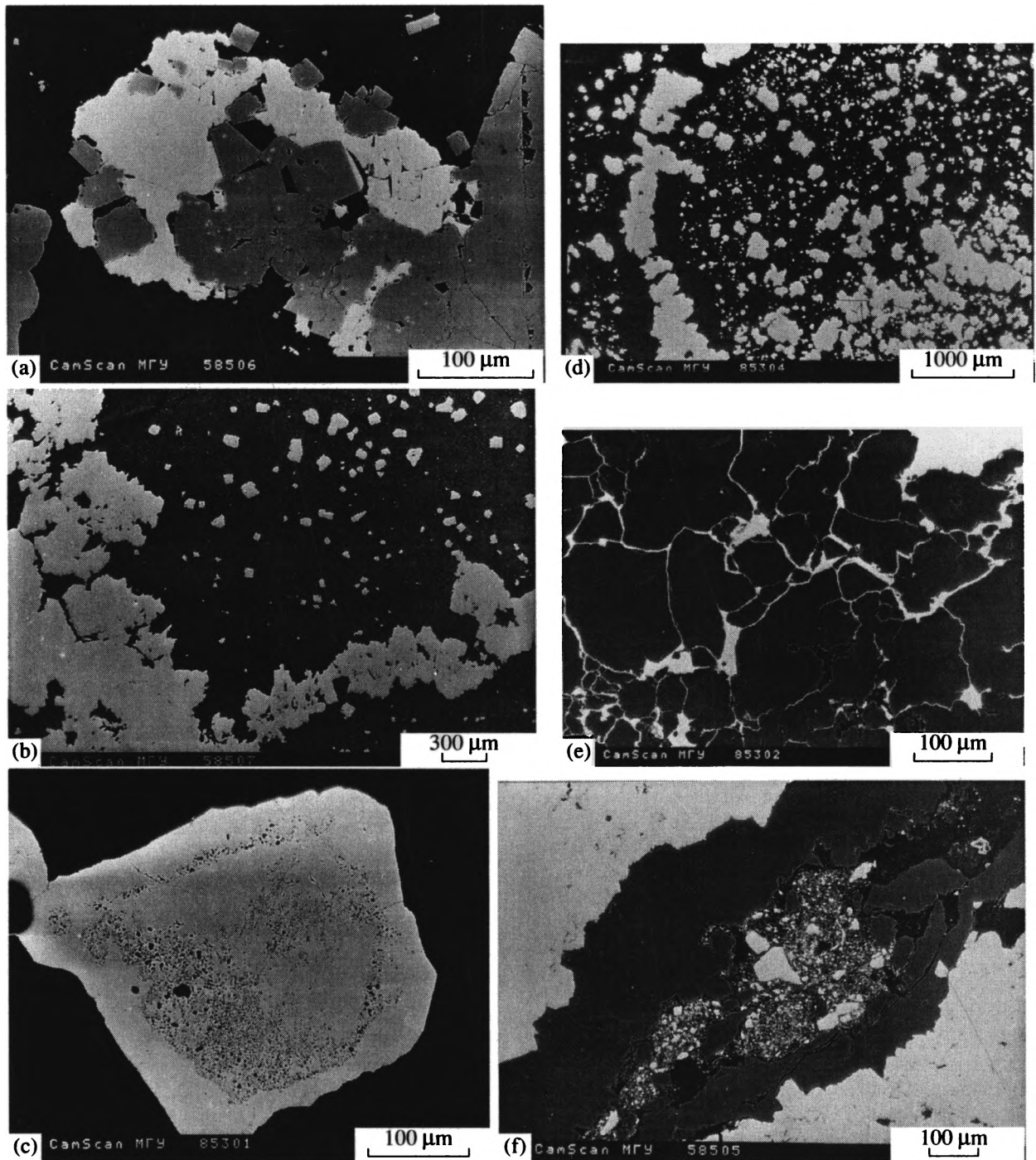


Fig. 10. Heterogeneous crystals and different types of structural relationships between minerals. Polished sections, reflected electron images. Sample H-9X-1.p.4 (depth 44.5 m): (a) replacement of coarse-crystalline pyrite (gray) by chalcopyrite (white) and redeposition of fine-grained euhedral cubic pyrite overgrown with chalcopyrite, (b) corrosion of coarse-crystalline pyrite by fine-crystalline quartz with neogenic fine-crystalline pyrite; (c) sample M-7R-1.p.1 (depth 34 m), zonal pyrite with a porous core and pure rim; (d) sample M-5R-1.p.8 (depth 25 m), pure quartz stringers with a chain of large pyrite grains in the center of a fine-crystalline pyrite-quartz aggregate; (e) sample M-3R-1.p.12 (depth 15 m), network of fine pyrite stringers (along quartz grain boundaries) with local swells and rare cubic metacrystals; (f) sample H-8N-1.p.7 (depth 41 m), crack in coarse-crystalline pyrite filled with quartz and fine-clastic pyrite in the center.

(>90%) assemblages. This kind of situation is common for hydrothermal oceanic mounds (Fouquet *et al.*, 1993; Herzig and Hannington, 1995; Mozgova *et al.*, 1998a; and others). As was demonstrated above, pyrite is the main carrier of Au in drill core samples, and sphalerite does not contain traces of this metal. Thus, when passing from the mound surface to deep zones, we can observe that the carrier of Au is replaced, indicating a considerable mobility and variation of geochemical bonds of this element. In contrast to Au, platinum group elements retain a stable association with zinc sulfides both on the surface (Crocket, 1990) and at depth (our data).

The vertical mineralogical–geochemical zonality in the TAG mound is supposed to be caused by a zonal purification owing to the mobilization of elements from older sulfides by high-temperature fluids and delivery to the surface, where the elements are redeposited during the mixing of solutions with cold seawater. This process is likely responsible for different types of Au distribution in zonal crystals or aggregates from deep and near-surface sections of holes. The behavior of Au and PGE in this process is different. Geochemical bonds of Au are more diverse. We believe that the horizontal mineralogical–geochemical zonality and replacement of mineral-carriers of maximal concentrations of Au in different zones of the inactive Mir mound (Mozgova *et al.*, 1997, 1998a, 1998b) were induced by a hydrothermal reworking of ores during the development of the horizontal infiltration–metasomatic zonality and a high mobility of Au. This conclusion fits the concept of zonal purification along the lateral direction.

The source of metals, including noble metals, in oceanic sulfide mounds is an essential problem in the theory of modern hydrothermal mineralization. However, this problem is debatable, and two alternative concepts are available. According to the first concept, metals are directly delivered from the mantle during its degassing. According to the second concept, metals are released during the interaction between high-temperature solutions and oceanic crust.

Butuzova (1998) scrutinized all *pro et contra* of these concepts and presented convincing evidences for the active extraction of a series of trace elements, including Au, Ag, and Hg from magma. Currently, the concept of the “mercury respiration of the Earth,” i.e., the mantle origin of Hg and its indicator role in deep fractures, has gained general recognition (Ozerova, 1986). The Au–Hg correlation, reported from continental deposits and several oceanic hydrothermal edifices, is considered evidence of the mantle source of Au (Mozgova *et al.*, 1997, 1998a, 1998b). The presence of elevated concentrations of Hg in drill core samples studied and its correlation with Au suggests a similar conclusion with respect to the TAG mound.

The concept of mantle source of Au for the TAG mound is in agreement with facts reported by other researchers. Based on a detailed geochemical study of

Table 3. Variation of maximal concentrations of Au (wt %) in sulfide aggregates vs. hole depth within the TAG mound

Depth, m	Sample no.	Pyrite aggregates and crystals		Chal- copyrite	Figure
		center	edge		
Hole 957H					
8.7	1N-1.p.2	0.17	0.12	0	7b
8.7	1N-1.p.2	0	n. d	0.15	7c
9	1N-1.p.9D	0	0.25	0	7e
41	8N-1.p.7	0.09	0	—	10f
41.5	8N-1.p.9	0.09	tr.	—	9c
41.5	9X-1.p.4	0.30	0	—	10b
Hole 957C					
11	4W-1.p1	0	0.09	0.35	7d
14	6W-1.p3	—	0.25	—	9a
21	7N-2.p.1D	tr.	0.14	0.14	7f
31	11N-1.p.2A	0.08	0	—	—
47	16N-1p.9	0.13	0	—	9d
47	16N-1p.9	0	0	—	—
Hole 957M					
1.5	1R-2p.2	0.10	0.09	—	—
1.6	1R-2p.6	0	0.13	—	8d
15	3R-1.p.12	0	0.14	—	8c
16	3R-1.p.27	0	0.20	—	—
25	5R-1.p.8	0.11	0.33	—	10d
26	5R-1.p.15	0.16	0	0	8b
34	7R-1.p.1	0.20	0	—	10c
38	8R-1.p.1	0.19	0	0.18	8a

Note: (–) Not analyzed.

core samples (Herzig *et al.*, 1998a), the Au content ranges from 60 mg/t in altered basalt from the mound basement to 1 mg/t in unaltered MORB rocks. Hence, basalt is enriched rather than depleted in Au during metamorphic alterations. According to Crocket (1990), a proponent for the concept of metal release from basalt, the Au/Ir ratio in surficial sulfide samples is equal to 1700–41000, which is approximately 100 times higher than the value for basalt (10–30). He attributed discrepancies mentioned above to the Au and Ir fractionation by various mechanisms during the mixing of high-temperature fluids with cold seawater and the subsequent sulfide deposition. These observations, however, can serve as optional evidence of the mantle source of Au.

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Geochemistry of Rare Earth Elements in Micro- and Macronodules from the Pacific Bioproductive Zone

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Abstract—Concentrations and compositions of rare earth elements (REE) in three micronodule fractions (50–250, 250–500, and >500 μm), coexisting macronodules, and host sediments are examined. The samples were collected from three sites (Guatemala Basin, Peru Basin, and northern equatorial Pacific) located in elevated bioproductivity zones of the surficial water. The influence of micronodule size is dominant for REE compositions and subordinate for REE concentrations. For example, the Ce concentration inversely correlates with the micronodule fraction dimension and drops to the lowest value in macronodules and host sediments. The Ce decrease is generally accompanied by the Mn/Fe increase in micro- and macronodules. Hence, the role of diagenetic source of material directly correlates with the micronodule dimension. The contribution of diagenetic source is maximal for macronodules. The REE signature distinctions of micronodules and macronodules can be attributed to variations of hydrogenic iron oxyhydroxides and diagenetic (hydrothermal) iron hydroxophosphates that are the major REE carriers in ferromanganese ore deposits. The relationship and general trend in the chemistry of coexisting macronodules suggest that they can represent products of the initial stage of nodule formation.

Rare earth elements (REE) are characterized by a unique similarity of chemical properties. They can evolve in accordance with the development of hydrothermal processes and indicate the source of material. Cerium and europium, which can exist in two oxidation states, serve as indicators of redox conditions in the environment. The REE composition is fractionated in oceanic water with a low amount of terrigenous material. The high stability of complex compounds of heavy rare earth elements (HREE) promotes their intense accumulation in the pelagic zone, relative to light rare earth elements (LREE). The negative Ce anomaly in oceanic water is a result of oxidation and active transition of this element into the suspension (Klinkhammer *et al.*, 1983; Masuzawa and Koyama, 1989; Bertram and Elderfield, 1993; Sholkovitz *et al.*, 1994; Zhang and Nozaki, 1996).

Iron and manganese oxyhydroxides are the main components of oceanic ferromanganese aggregates (macronodules, micronodules, and crusts). Rare earth elements are not found as individual phases in ferromanganese deposits. Most researchers believe that these components are related to the ferrous oxyhydroxide component of crusts and macronodules (Dubinin and Volkov, 1989). Although oceanic water is the main source of REE in iron oxyhydroxides, the REE composition depends on the genesis of oxyhydroxides in ocean. Hydrogenic pelagic macronodules and crusts have a positive Ce anomaly and are commonly enriched in LREE or IREE, relative to the NASC value (Piper, 1974; Toth, 1980; Aplin, 1984; Hein *et al.*, 1988; Koski, 1988; De Carlo, 1991). Hydrothermal iron oxyhydrox-

ides are characterized by the negative Ce anomaly and LREE deficit. This type of REE signature is typical of metalliferous sediments, associated macronodules, and fast-growing Mn-rich crusts that are abundant around hydrothermal sources in the ocean (Piper and Graef, 1974; Toth, 1980; Burnett and Piper, 1977; Elderfield and Greaves, 1981; Clauer *et al.*, 1984; Murphy and Dymond, 1984; Dubinin and Volkov, 1986; Volkov and Dubinin, 1987; Dubinin, 1996).

Host sediments, pore water, and bottom water are considered as the sources of material for oceanic macronodules. The study of REE composition in the reactive part of sediments in macronodules suggest an involvement of sediments in the material supply during the nodule growth (Elderfield *et al.*, 1981; Dubinin, 1996). In hydrothermal districts (Bauer Depression and Guatemala Basin in the Pacific), the REE pattern in macronodules is typical of oceanic (hydrothermal sedimentary) ferromanganese aggregates (Elderfield and Greaves, 1981; Murphy and Dymond, 1984; Dubinin, 1996). However, in many cases (e.g., Bellingshausen Basin, Peru Basin, and the northern equatorial Pacific), sediments with the negative Ce anomaly contain macronodules with the positive Ce anomaly (Girin *et al.*, 1979; Courtois and Clauer, 1980; Glasby *et al.*, 1987; Dubinin and Strekopytov, 1994).

Micronodules and macronodules are similar in the chemical composition, mineralogy, and morphology. They are elsewhere encountered in oxidized pelagic sediments, and their concentration inversely correlates with sedimentation rate (Stoffers *et al.*, 1984, 1985; Sval'nov *et al.*, 1991a, 1991b; Pattan, 1993). The

Table 1. Location of stations and certain lithological and geochemical characteristics of bottom sediments

Station	Horizon, cm	Coordinates		Depth, m	Sediment type	CaCO ₃ , %	C _{org} , %	Micronodule fraction distribution (% of the total mass)		
								I	II	III
3874	0–2	92°46.95' W	06°30.2' N	3610	CS	1.6	0.65	29	45	26
56	0–6	86°00' W	13°15' S	4600	C	13	0.44	29	51	20
3834	56–62	120°28.7' W	07°40.8' N	3850	PCZ	<1	0.09	46	15	39
3834	65–70	120°28.7' W	07°40.8' N	3850	PCZ	<1	0.07	78	20	2

Note: Micronodule fractions, μm (here and in Tables 2, 3, and 5): (I) 50–250, (II) 250–500, (III) >500; (CS) clayey–radiolarian ooze; (C) clayey mud; (PCZ) pelagic clay with zeolite.

micronodule–nodule transition is not gradational (Kunzendorf *et al.*, 1989). Macronodules and micronodules have different compositions. Relative to macronodules, some micronodules are characterized by higher values of the Mg/Fe ratio, Ce anomaly, and Co content, whereas other micronodules demonstrate the opposite relationships (Addy, 1979; Kunzendorf *et al.*, 1989; Pattan *et al.*, 1994; Dubinin and Sval'nov, 1995). The study of Guatemala Basin sediments has revealed a gradual evolution of the Ce anomaly in fine- and coarse-grained sediments, macronodules, and the reactive part of sediments. The fine fraction is the closest compositional analogue of the hydrogenic background and ferromanganese crusts dredged in the region (Dubinin and Sval'nov, 1996). Hence, micro- and macronodules represent the transitional coarse-grained series between hydrogenic fine micronodules and reactive sediments. This type of REE distribution is indicative of a high mobility of hydrogenic particles of ferromanganese oxyhydroxides at the initial stage of micronodule growth during the diagenetic reaction at the water–bottom interface.

This work scrutinizes the REE behavior in different micronodule fractions and associated macronodules in oceanic areas where the bioproductivity is high and the hydrothermal impact on bottom sediments is significant.

MATERIALS AND METHODS

The studied sediments were collected from Station 3874 (Guatemala Basin), Station 56 (Peru Basin), and Station 3834 (northern equatorial zone of the Pacific). Coordinates and depths of stations, horizons of sediments, and their lithological types are given in Table 1.

The drag sample, collected from Station 3874 in the MANOP Site H area (Dymond *et al.*, 1984; Dubinin, 1996; Dubinin and Sval'nov, 1996), represents miopelagic clayey–radiolarian oozes and ferromanganese nodules with a productivity of 24.6 kg/m². Micronodules were separated under a binocular microscope from the washed sample of surficial sediment (horizon 0–2 cm) and then successively passed through three (50–250, 250–500, and >500 μm) sieves. The mass propor-

tion of obtained fractions is shown in Table 1. The drag sample (horizon 0–6 cm) from Station 56 represents miopelagic clay containing 14–20% CaCO₃ and abundant nodules. Nodules are characterized by polynucleus, discoid, and ellipsoid forms. Micronodules, separated from the surficial (0–6 cm) sediment, are also composed of different fractions (Table 1). At Station 3834, micronodules were collected from two horizons (55–57 and 65–67 cm) of pre-Pleistocene pelagic (zeolite–clayey) sediments. The upper (55–57 cm) horizon is located immediately below the hiatus boundary (Sval'nov, 1991; Sval'nov *et al.*, 1991a). The mass proportion of micronodules at this horizon (Table 1) shows that the coarse fraction differs from the finer variety and consists of dendritic aggregates confined to the upper boundary of the interval.

Micronodules, macronodules, and host sediments (~50 mg) were processed in a 20 ml solution of 1 M NH₂OH · HCl + 25% CH₃COOH (Chester and Hughes, 1967) for 4 h. Bulk samples and Chester leachate residues were decomposed in platinum dishes with a mixture of concentrated HF + HClO₄. The samples prepared for analysis represented 5% HNO₃ solutions. The REE analysis was carried out with a ICP-MS (PlasmaQuad PQ2+) device equipped with two internal standards of In and Re. The analytical method is scrutinized in (Dubinin, 1993). The standard deviation did not exceed 5%. Concentrations of Fe, Mn, Al, Co, Ni, and Cu were determined in the same samples by the atomic absorption spectrometry with an accuracy of 3–5%. The P concentration was measured by spectrophotometry with an accuracy of ~3%.

RESULTS

Station 3874. As is evident from Table 2, sediments from this station are enriched in Mn (4.13%). This specific feature of surficial sediments from the Guatemala Basin was reported earlier (Graybeal and Heath, 1984; Morozov, 1995). A high Mn concentration is observed in the ore portion of macronodules and in all fractions of micronodules. Micronodules, macronodules, and sediments are depleted in Ce and LREE. According to Dubinin (1996), this feature is typical of hydrothermal

Table 2. Composition of sediments from Station 3874 before and after treatment with 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 25% CH_3COOH

Element	Sediment (0–2 cm)		Nodule		Micronodule fractions					
					I		II		III	
	1	2	1	2	2	3	2	3	2	3
La	31.0	21.6	29.7	24.9	19.1	2.16	18.0	2.02	19.9	3.88
Ce	34.2	19.6	32.2	27.5	33.9	3.92	27.6	3.60	25.3	7.11
Pr	6.85	4.43	5.76	5.06	4.33	0.43	4.06	0.46	4.40	0.86
Nd	29.4	21.2	25.4	22.7	18.0	1.90	17.3	1.77	18.7	3.32
Sm	6.62	4.31	5.44	5.04	3.84	0.56	3.86	0.50	4.32	0.79
Eu	1.61	1.20	1.52	1.30	0.95	0.18	1.02	0.11	1.09	0.21
Gd	7.06	5.72	6.26	6.01	4.15	0.48	3.93	0.36	4.77	0.42
Tb	1.11	0.87	1.08	0.96	0.67	0.07	0.64	0.06	0.71	0.08
Dy	8.11	6.04	7.08	6.24	4.42	0.38	4.21	n. d.	4.70	1.06
Ho	1.72	1.39	1.47	1.39	0.97	0.08	0.92	0.07	1.04	0.10
Er	5.76	4.08	4.58	4.14	2.96	0.24	2.80	0.24	3.20	0.34
Tm	0.83	0.64	0.71	0.64	0.42	n. d.	0.41	0.04	0.48	0.05
Yb	5.09	4.10	4.40	4.14	2.98	0.23	2.83	0.26	3.26	0.35
Lu	0.75	0.66	0.68	0.64	0.47	0.03	0.44	0.04	0.51	0.05
Fe	4.69	1.34	2.55	1.85	1.75	0.56	1.34	0.45	1.19	0.62
Mn	4.13	3.88	41.0	40.0	36.3	0.19	37.6	0.07	36.8	0.06
Al	5.08	0.69	1.29	0.47	0.63	0.59	0.54	0.62	0.43	0.76
P	0.18	0.135	0.15	0.076	0.126	0.009	0.157	0.008	0.156	0.011
Co	0.005	n. a.	0.02	n. a.	0.033	n. d.	0.020	n. a.	n. d.	n. a.
Ni	0.056	n. a.	0.75	n. a.	0.97	0.02	1.04	n. a.	1.03	n. a.
Cu	0.056	n. a.	0.315	n. a.	0.49	0.05	0.47	n. a.	0.40	n. a.
Mn/Fe	0.9	2.9	16.1	21.6	20.7	0.3	28.1	0.1	31.0	0.1
Ni/Cu	1.00	–	2.38	–	1.98	0.38	2.22	–	2.59	–
Ce/Ce*	0.50	0.41	0.52	0.51	0.81	0.86	0.69	0.84	0.58	0.88
LREE/HREE	0.42	0.36	0.43	0.41	0.46	0.69	0.46	0.54	0.44	0.80

Note: (1) Total concentration; (2) leachate; (3) residue; (n. d.) not detected; (n. a.) not analyzed. $\text{Ce/Ce}^* = 2\text{Ce}^{\text{N}}/(\text{La}^{\text{N}} + \text{Nd}^{\text{N}})$; $\text{LREE/HREE} = (\text{La}^{\text{N}} + \text{Pr}^{\text{N}} + \text{Nd}^{\text{N}})/(\text{Er}^{\text{N}} + \text{Tm}^{\text{N}} + \text{Yb}^{\text{N}} + \text{Lu}^{\text{N}})$, where La^{N} , Pr^{N} , etc. represent NASC-normalized concentrations of respective rare earth elements (Gromet *et al.*, 1984). REE concentrations are given in ppm, other elements are given in %.

zone sediments (Fig. 1). The overall REE concentration is moderate; therefore, difficulties emerge when we have to determine the REE portion connected with the nonhydroxide matrix. This problem is urgent for micronodules, since the probability of a significant influence of nonhydroxide nuclei is high (Sval'nov *et al.*, 1991b). The impact of nonhydroxide material on the REE composition was suppressed by processing micronodules, macronodules, and host sediments with a mixture of hydrochloric hydroxylamine (1M $\text{NH}_2\text{OH} \cdot \text{HCl}$) and acetic acid (25% CH_3COOH). According to (Chester and Hughes, 1967), this mixture can extract poorly crystallized ferromanganese oxyhydroxides and does not destroy the aluminosilicate matrix of sediments. Element concentrations in micronodule leachates, relative to total concentrations, were calculated according to formulae $E^{\text{ch}}/(E^{\text{ch}} + E^{\text{res}})$ (for micronodules) and

$E^{\text{ch}}/E^{\text{tot}}$ (for macronodules and host sediments), where E^{ch} is the element concentration in the Chester leachate, E^{res} is the element concentration in the Chester leachate residue, and E^{tot} is the total element concentration.

Macro- and micronodules (henceforth, nodules) yield an almost equal amount of Fe (65.8–75.8%) and almost 100% Mn. The Al extraction into leachate decreases from 51.6% in fine micronodules to 36% in macronodules and 13.6% in host sediments. The P extraction is 93–95% from micronodules, 51% from macronodules, and 75% from host sediments. The average REE extraction is as much as 84–90% from all nodule fractions and 68% from host sediments. In all cases, the leachate is depleted in LREE, relative to bulk samples (Fig. 2). The REE composition in leachates and bulk samples regularly changes in the following series:

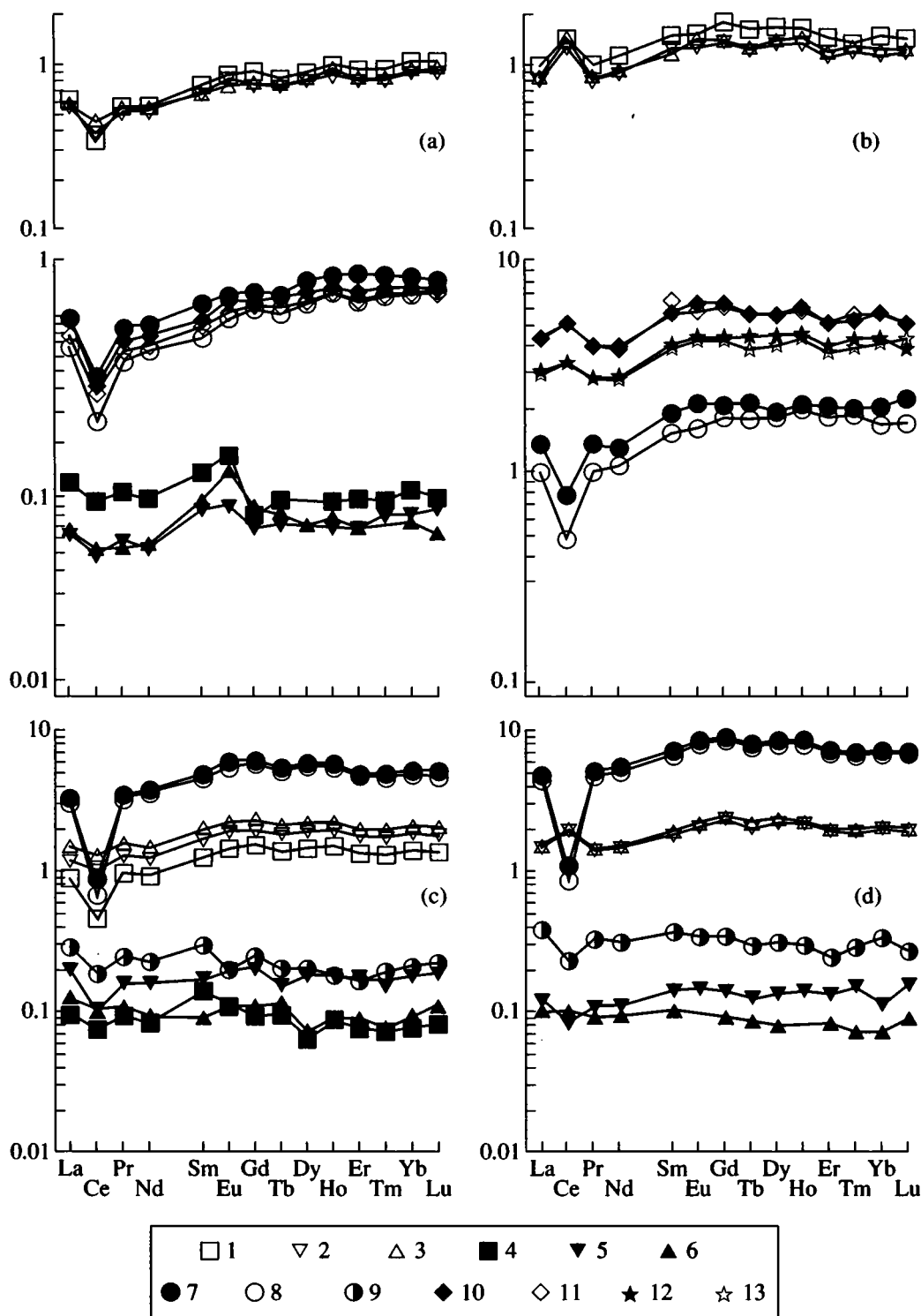


Fig. 1. The NASC-normalized (Gromet *et al.*, 1984) compositions of REE in sediments from (a) Station 3874, (b) Station 56; (c) Station 3834 (horizon 55–62 cm), and (d) Station 3834 (horizon 65–70 cm). Chester leachate fractions of micronodules (μm): (1) 50–250, (2) 250–500, (3) >500; residue fractions: (4) 50–250, (5) 250–500, (6) >500; host sediments: (7) bulk sample, (8) Chester leachate, (9) residue; macronodules: (10) bulk sample from the upper section, (11) Chester leachate from the upper section, (12) bulk sample from the lower section, (13) Chester leachate from the lower section. In the case of sediments from Station 3874, (12) and (13) correspond to REE compositions of the bulk sample and its Chester leachate, respectively.

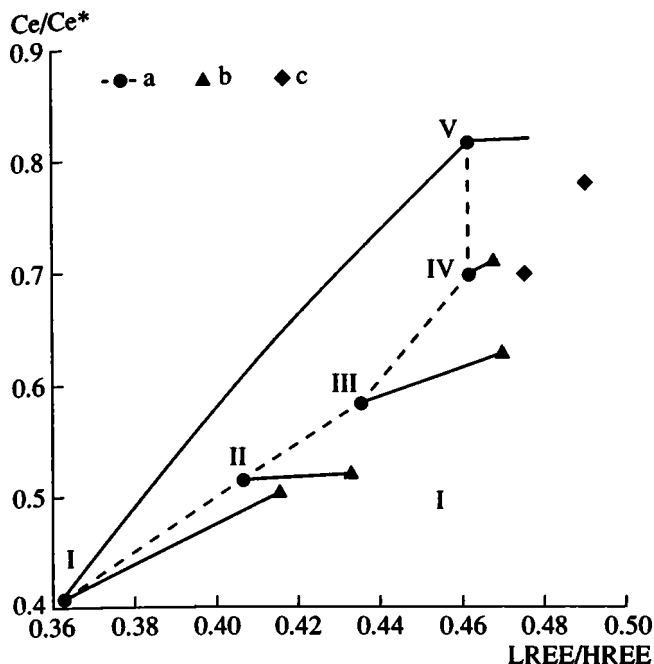


Fig. 2. REE compositions of sediments from Station 3874 in Ce/Ce^* –LREE/HREE coordinates. (I) Sediment; (II) FMN; micronodule fractions (μm): (III) >500 , (IV) 250–500, (V) 50–250; (a) Chester leachates; (b) bulk samples; (c) hydrogenic crusts from the MANOP Site H (Murphy and Dymond, 1984). The line across data points of Chester leachates from host sediment and 50–250 μm -fraction micronodule (I–V) show the REE composition variations in the mixing model.

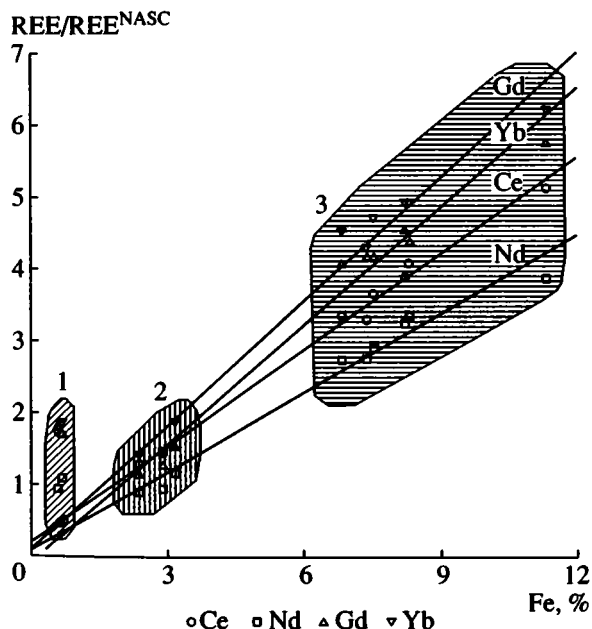


Fig. 3. The NASC-normalized REE concentration vs. Fe concentration in sediments from Station 56. (1) Reactive portion of sediments; (2) Chester leachate from micronodules; (3) leachates from upper and lower sections of the FMN (Dubinin and Strekopytov, 1994).

fine micronodules (50–250 μm)–medium micronodules (250–500 μm)–coarse macronodules ($>500 \mu m$)–host sediments. Maximal Ce and LREE concentrations are observed in the finest micronodule fraction (Fig. 2). The REE signature of sediments is apparently governed by the reactive portion of samples characterized by more appreciable differences in terms of the REE composition.

Station 56. Compositions of nodules and host sediments from this station are given in Table 3. Relative to counterparts from Station 3874, sediments here are depleted in Mn. At a depth of 6–10 cm, the Mn concentration decreases to 0.36% (Dubinin and Strekopytov, 1994), suggesting the existence of suboxidative conditions. The reactive portion of micronodules is enriched in Mn. The Mn/Fe value is equal to 11–14 in micronodules and 2.1–3.4 in macronodules. These values match the data reported in (Stoffers *et al.*, 1984; Kunzendorf *et al.*, 1989). The REE concentration correlates with the Fe concentration (Dubinin and Strekopytov, 1994). Therefore, relative to macronodules, micronodules are depleted in REE (Fig. 3). The positive Ce anomaly is stronger in micronodules, relative to macronodules. Moreover, the anomaly is more pronounced in the finer fractions (Figs. 1, 4). Host sediments, particularly their reactive portion, have a negative Ce anomaly. The Ce anomaly is decreased in the coarser fragments and reactive portion of host sediments (Fig. 4). Thus, relationships between nodules and host sediments are similar at stations 56 and 3874 (Fig. 4). Distinctions in the positive Ce anomaly of nodules at these stations are

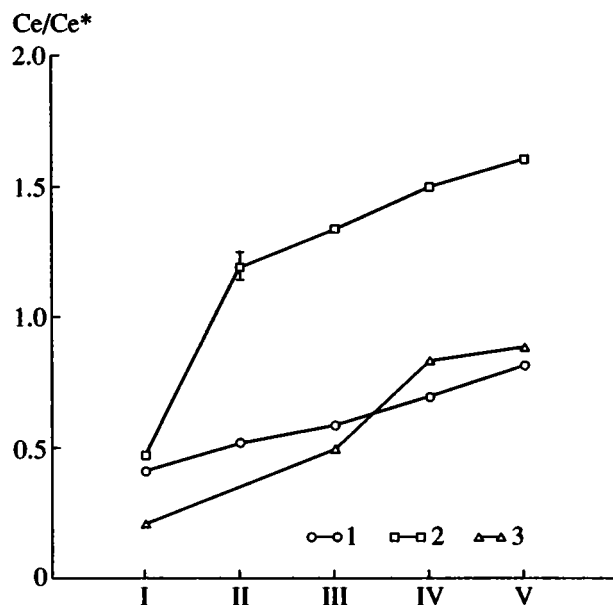


Fig. 4. Ce/Ce^* vs. reactive capacity and fraction dimension. (I) Host sediment, (II) macronodules, (III–V) micronodules. Stations: (1) 3874; (2) 56; (3) 3834.

Table 3. Composition of sediments from Station 56 before and after treatment with 1M $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 25% CH_3COOH

Element	Sediment		Nodule				Micronodule fractions		
	(0–1 cm)		top		bottom		I	II	III
	1	2	1	2	1	2	2	2	2
La	43.5	32.0	96.2	93.0	138	139	28.1	26.1	32.3
Ce	57.0	35.3	242	240	375	373	107	94.1	106
Pr	10.8	8.0	21.9	22.0	31.7	31.6	6.77	6.37	8.01
Nd	43.4	35.7	93.9	91.0	132	127	31.4	29.9	38.5
Sm	11.0	8.8	23.1	22.2	32.7	32.6	6.73	7.25	8.72
Eu	2.66	2.02	5.41	5.24	7.82	7.18	1.81	1.59	1.94
Gd	10.9	9.57	22.8	22.2	33.4	32.1	7.47	7.28	9.65
Tb	1.83	1.53	3.77	3.25	4.87	4.86	1.10	1.07	1.42
Dy	10.2	9.62	23.4	20.9	29.6	29.6	7.42	7.01	9.01
Ho	2.21	2.09	4.77	4.58	6.18	6.38	1.59	1.44	1.78
Er	7.11	6.31	13.6	12.8	17.9	17.7	4.19	3.79	5.07
Tm	1.02	0.95	2.17	1.96	2.67	2.88	0.67	0.61	0.69
Yb	6.46	5.33	13.6	12.9	18.2	17.8	4.00	3.59	4.79
Lu	1.09	0.84	1.87	2.10	2.50	2.50	0.62	0.59	0.71
Fe	4.37	0.66	8.60	7.38	12.6	11.3	2.87	2.37	3.14
Mn	0.77	0.68	26.2	25.4	23.8	23.5	33.7	34.0	34.1
Al	6.16	0.47	2.31	0.98	1.45	0.70	0.77	0.70	0.92
P	0.19	0.13	0.21	0.178	0.30	0.238	0.121	0.116	0.126
Co	n. a.	n. a.	0.10	n. a.	0.15	n. a.	n. d.	0.002	0.03
Ni	n. a.	n. a.	1.30	n. a.	1.03	n. a.	1.34	1.27	1.53
Cu	n. a.	n. a.	0.64	n. a.	0.44	n. a.	1.16	0.95	0.98
Mn/Fe	0.2	1.0	3.0	3.4	1.9	2.1	11.7	14.3	10.9
Ni/Cu	–	–	2.03	–	2.34	–	1.16	1.34	1.56
Ce/Ce*	0.58	0.46	1.13	1.16	1.24	1.25	1.60	1.50	1.33
LREE/HREE	0.48	0.43	0.52	0.52	0.57	0.56	0.52	0.54	0.54

Note: (1) Total concentration; (2) leachate; (n. d.) not detected; (n. a.) not analyzed. REE concentrations are given in ppm, other elements are given in %.

caused by a deeper pelagic environment of the Peru Basin. This conclusion is based on the comparison of sedimentation rates varying from 2.3–15 mm/ka in the Guatemala Basin to 1–5 mm/ka in the Peru Basin (Bogdanov and Chekhovskikh, 1979; Kadko and Heath, 1984; Stoffers *et al.*, 1984; Skornyakova *et al.*, 1993).

Station 3834. Samples from this station are represented by pelagic zeolite–clayey sediments with a high Mn concentration. The Mn concentration is as much as 14.1% at the upper (56–62 cm) horizon and 4.5% at the lower (65–70 cm) horizon (Table 4). The Cu, Ni, and P contents are enhanced. The REE concentration is also higher in sediments, relative to the NASC value. The Ce anomaly is negative (Fig. 1). Based on a comparative analysis of the reactive portion and bulk composition of sediments (Table 4), as much as 98% Mn can be

extracted into the leachate. The Fe extraction equals to 14% at the upper horizon and 9% at the lower horizon. Respective values for Al are 13 and 8%. The extraction of Ni, Co, Cu, and P is almost 100%. The extraction of REE, except Ce, is as high as 92–97%, and the leachate contains more HREE than LREE.

As is evident from the compositional data (Table 5), micromodules from this station have a high Mn/Fe value. At the upper horizon, the fine fraction is characterized by a lower value of this ratio, relative to the coarse fraction. The relative concentration of Fe in the leachate decreases from 44% in the coarse fraction to 21% in the fine fraction at 55–57 cm. The respective values are equal to 54 and 43% at 65–67 cm. The Al behavior is similar and suggests that a part of the reactive Fe can occur in aluminosilicates. The P extraction varies from 92 to 100%. Elements, such as Mn, Co, Ni,

Table 4. Composition of sediments from Station 3834 before and after treatment with 1M NH₂OH · HCl + 25% CH₃COOH

Element	Horizon 56–62 cm				Horizon 65–70 cm			
	1	2	3	4	1	2	3	4
La	95.6	9.24	105	105	143	12.0	155	155
Ce	49.3	13.5	62.9	63.1	61.9	16.6	78.5	79.9
Pr	25.6	1.91	27.6	27.5	37.4	2.57	39.9	40.4
Nd	118	7.37	125	125	170	10.0	180	183
Sm	26.2	1.67	27.9	28.1	38.2	2.08	40.2	41.0
Eu	6.77	0.24	7.01	7.47	9.99	0.42	10.4	10.6
Gd	30.5	1.29	31.8	32.0	44.7	1.77	46.5	47.2
Tb	4.40	0.17	4.57	4.64	6.57	0.25	6.82	6.82
Dy	29.2	1.05	30.3	30.6	41.7	1.61	43.3	44.1
Ho	5.73	0.19	5.92	6.02	8.45	0.31	8.76	8.96
Er	16.5	0.55	17.0	16.8	23.6	0.83	24.4	24.8
Tm	2.33	0.10	2.43	2.47	3.36	0.14	3.50	3.52
Yb	15.1	0.66	15.7	16.1	21.2	1.03	22.3	22.8
Lu	2.26	0.11	2.37	2.50	3.32	0.13	3.45	3.44
Fe	0.60	3.62	4.22	4.19	0.52	4.99	5.50	5.39
Mn	14.0	0.09	14.1	13.9	4.32	0.07	4.39	4.54
Al	0.61	4.07	4.68	4.54	0.46	5.17	5.63	5.30
P	0.340	0.003	0.343	0.332	0.476	n. d.	0.476	0.454
Co	0.021	n. d.	0.021	0.018	0.005	n. d.	0.005	0.019
Ni	0.517	0.012	0.529	0.507	0.212	0.004	0.216	0.227
Cu	0.423	0.035	0.458	0.453	0.150	0.046	0.196	0.193
Mn/Fe	23.5	0.03	3.35	3.32	8.37	0.01	0.80	0.84
Ni/Cu	1.22	0.34	1.16	1.12	1.41	0.09	1.10	1.18
Ce/Ce*	0.21	0.72	0.24	0.24	0.18	0.67	0.21	0.21
LREE/HREE	0.51	0.95	0.53	0.52	0.52	0.89	0.54	0.54

Note: (1) Leachate; (2) residue; (3) leachate + residue; (4) total content; (n. d.) not detected. REE concentrations are given in ppm, other elements are given in %.

and Cu are also almost completely extracted into the leachate. The reactive Fe concentration directly correlates with REE concentrations. Irrespective of horizons and fractions, the REE concentration in leachate ranges from 86 to 100%, relative to the total concentration of leachate and residue. The negative Ce anomaly pattern is similar (Figs. 1, 4). Among micronodules from Station 3834, the REE(III) concentration is higher in the 250–500- μ m fraction at the lower (65–67 cm) horizon. The REE composition in micronodules from lower and upper horizons of this station reveals a positive Ce anomaly. The reactive portion of host sediments and micronodules from both horizons is characterized by significant correlations in the Fe–Ce, Mn–Cu–Ni, and P–REE(III) systems. However, the P–REE(III) correlation disappears, if only micronodules are considered (Fig. 5). At the higher (55–57 cm) horizon, fine micronodule fractions are marked by a higher Ce anomaly, relative to the reactive portion of sediments (Fig. 4). As

was mentioned above, this regularity is typical of micronodules from stations 3874 and 56.

DISCUSSION

In sediments from all of the stations studied, the REE signature of larger micronodules is similar to that of macronodules and reactive sediments (Fig. 4). We suppose that this phenomenon can provide an insight into the initial scenario of the formation of authigenic ferromanganese oxyhydroxides in sediments. Since rare earth elements do not form phases of their own in nodules and host sediments, we should identify key phases that govern the REE composition of sediments.

All of the studied stations are located near the East Pacific Rise. Therefore, sediments in this region can contain hydrothermal material (ferromanganese oxyhydroxides). According to several works (Graybeal and Heath, 1984; Dubinin, 1996; Dubinin and Sval'nov,

Table 5. Compositions of micronodules from Station 3834

Element	Horizon 55–57 cm						Horizon 65–67 cm			
	I		II		III		I		II	
	1	2	1	2	1	2	1	2	1	2
La	48.5	4.08	37.4	6.17	28.3	3.19	49.0	3.25	46.4	3.71
Ce	96.2	7.41	72.4	7.34	33.4	5.45	145	7.25	138	6.00
Pr	12.4	0.85	10.1	1.23	7.58	0.73	11.3	0.72	10.8	0.85
Nd	48.3	3.02	40.2	5.21	30.2	2.71	49.8	3.04	47.6	3.59
Sm	11.2	0.53	9.53	0.96	7.01	0.80	11.1	0.58	10.1	0.78
Eu	2.78	0.13	2.38	0.24	1.78	0.14	2.80	n. d.	2.53	0.18
Gd	12.0	0.56	10.0	1.05	7.99	0.48	12.7	0.47	12.1	0.72
Tb	1.80	0.10	1.51	0.13	1.18	0.08	1.91	0.07	1.69	0.10
Dy	11.4	0.37	9.81	0.94	7.50	0.33	12.4	0.41	11.3	0.68
Ho	2.30	0.09	2.00	0.19	1.56	0.09	2.36	0.09	2.28	0.14
Er	6.65	0.31	5.85	0.59	4.52	0.26	6.81	0.28	6.50	0.45
Tm	0.98	0.04	0.86	0.08	0.65	0.04	1.00	0.04	0.92	0.07
Yb	6.47	0.29	5.70	0.55	4.31	0.24	6.42	0.23	6.13	0.34
Lu	1.00	0.05	0.85	0.09	0.65	0.04	0.98	0.04	0.90	0.07
Fe	1.03	1.28	0.65	1.67	0.31	1.19	1.09	0.92	0.95	1.24
Mn	30.8	0.08	30.8	0.10	36.5	0.11	33.3	0.10	33.6	0.11
Al	0.96	1.55	0.86	1.54	0.48	1.23	0.72	1.00	0.64	1.28
P	0.180	0.007	0.191	0.014	0.123	0.005	0.116	n. d.	0.083	0.007
Co	0.074	n. a.	0.051	n. a.	0.008	n. a.	0.045	n. d.	0.032	n. d.
Ni	1.25	n. a.	1.10	n. a.	1.33	n. a.	1.72	0.004	1.59	0.008
Cu	1.07	n. a.	1.05	n. a.	1.10	n. a.	1.15	0.014	1.14	0.020
Mn/Fe	30	–	47	–	116	–	30.5	–	35.5	–
Ni/Cu	1.17	–	1.05	–	1.21	–	1.49	–	1.40	–
Ce/Ce*	0.88	0.93	0.83	0.57	0.51	0.82	1.31	1.03	1.30	0.73
LREE/HREE	0.74	1.14	0.69	0.95	0.68	1.17	0.74	1.19	0.75	0.81

Note: (1) Total concentration; (2) leachate; (n. d.) not detected; (n. a.) not analyzed. REE concentrations are given in ppm, other elements are given in %.

1996), the Mn abundance in Guatemala Basin surficial sediments is related to the hydrothermal delivery of material from the Galapagos spreading center. The REE composition in suspension (Murphy and Dymond, 1984), nodules, and host sediments indicates the presence of a negative Ce anomaly and LREE deficit in hydrothermal sediments of the ocean. Based on the distribution of REE and macrocomponents in Guatemala Basin sediments, rare earth elements (e.g., La) are linked to hydrothermal iron oxyhydroxides (Fig. 6), which derive REE from the suspension of this compound with Fe(III) in the bottom water (German *et al.*, 1990).

The Mn accumulation in surficial sediment layer is related to an intense delivery of this metal from the hydrothermal source and its mobilization from sediments due to the reduction by organic matter and the

subsequent oxidation of Mn by oxygen of bottom water. In Guatemala Basin sediments with an excess concentration of oxidizer (MnO_2), the early diagenetic reduction is limited by the reduction of Mn(IV) into Mn(II). Thus, during the early diagenetic redistribution, Fe can only be introduced into nodules in the form of colloid oxyhydroxides of Fe(III). The absorbed REE assemblage is retained during the process. The high intensity of reduction, transportation to the sediment surface, and oxidation of Mn by the dissolved oxygen results in the formation of Mn-rich nodules, in which the Fe concentration rarely exceeds 3% (Dymond *et al.*, 1984; Murphy and Dymond, 1984; Dubinin, 1996). The direct delivery of ferromanganese oxyhydroxides into nodules from bottom waters is responsible for the compositional asymmetry; relative to the lower section, the upper section of the nodule ore shell is thinner and

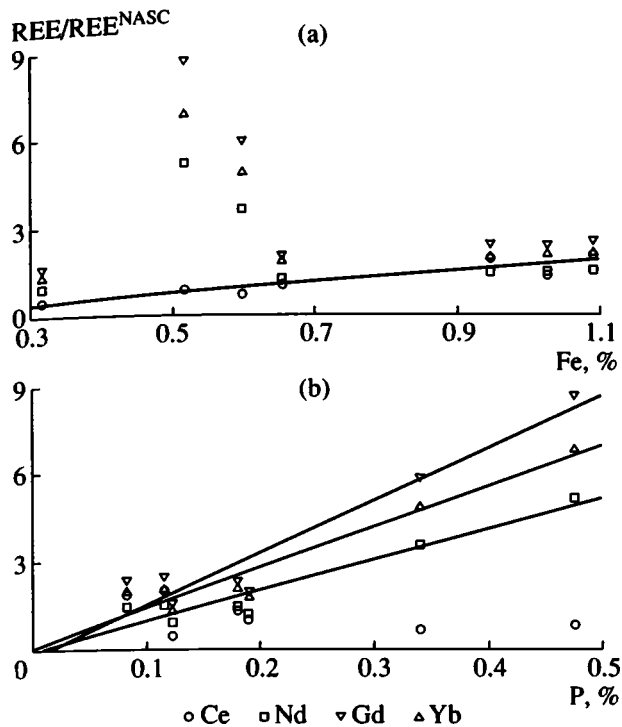


Fig. 5. The NASC-normalized REE vs. composition of the reactive portion of micronodules and host sediments from Station 3834. (a) Fe, (b) P.

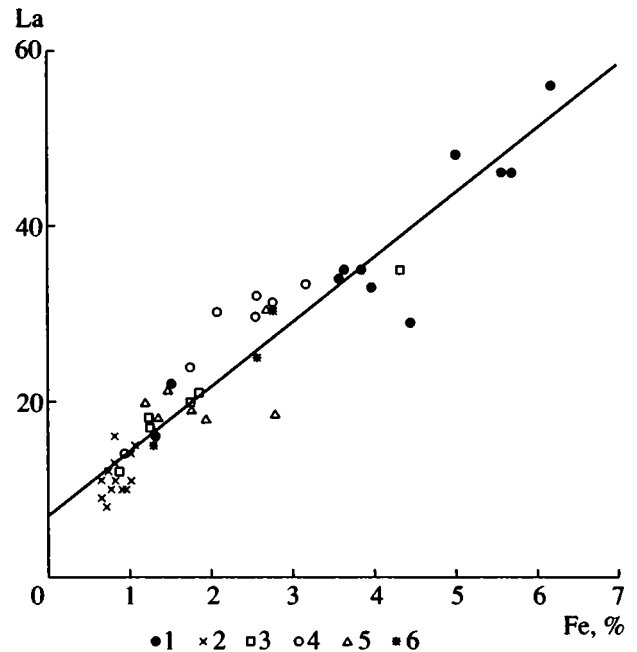


Fig. 6. REE (ppm) vs. Fe (%) in Guatemala Basin nodules. (1) Upper section of nodules; (2) lower section of nodules; (3) bulk samples of nodules (Murphy and Dymond, 1984); (4) bulk samples of nodules (Dubinin, 1996); (5) micronodule leachates (Dubinin and Sval'nov, 1995, 1996); (6) buried nodules (Dubinin, 1994).

enriched in Fe and REE. The Ce anomaly is higher in the upper sections of nodules (Fig. 7).

The comparative analysis of REE distribution in coexisting micro- and macronodules has revealed that the Ce anomaly is stronger in micronodules (Dubinin and Sval'nov, 1995). This statement is valid for Station 3874 as well. Hydrogenic crust samples dredged at the MANOP Site H are enriched in REE, relative to Fe (Murphy and Dymond, 1984). Nevertheless, they are closer to fine micronodules in terms of the REE composition (Dubinin and Sval'nov, 1996). Hence, one can assume that fine micronodules represent a better representative of hydrogenic segregations than the larger nodules.

If micronodules are formed in the uppermost, very thin sediment layer, hydrogenic rather than hydrothermal iron oxyhydroxides predominate at the earliest stage of nodule development. We assume that the above phenomenon is related to different structures of suspended particles of hydrothermal and hydrogenic ferromanganese oxyhydroxides. Since hydrothermal and hydrogenic particles are not separated by any distinct compositional boundaries (Fleet, 1984; German *et al.*, 1990), the composition of larger micronodules from Station 3874 gradually approaches the reactive portion of sediments, reflecting the general hydrothermal sedimentary background in the region.

The coarsening of micronodules is accompanied by the Mn/Fe ratio growth, suggesting an intense supply of

the reduced Mn from sediments. The intensification of the role of suboxidative diagenesis in the material supply in coarser micronodules is suggested by variations in the supply of the Mn-group microelements: Co is decreased, the Ni/Cu value is increased, and Cu and Ni are introduced into manganese oxyhydroxides. According to Dymond *et al.* (1984), Cu is more readily released than Ni during the suboxidative diagenesis, since Ni is preferentially introduced into the structure of manganese minerals. Lower sections of Guatemala Basin nodules with a higher Mn/Fe ratio are indeed enriched in Ni. The Ni/Cu versus Ce/Ce* plot (Fig. 8) shows the compositional variation in micronodules of different dimensions and nodules from the MANOP Site H. Figures 7 and 8 demonstrate that both ferruginous and manganous components of oxyhydroxides are altered during the growth of nodules. These compositional transformations are not connected with a simple mixing of hydrogenic and diagenetic materials (Fig. 2). They are caused by the prevalence of hydrogenic material at the micronodule-forming stage and the supply of material primarily from the underlying sediment. Thus, we can affirm that micronodules were formed at the water-seafloor interface during postsedimentary diagenetic alterations of the sediment. The subsequent compositional evolution is mainly induced by the delivery of reactive sediment, which is the major component of macronodules.

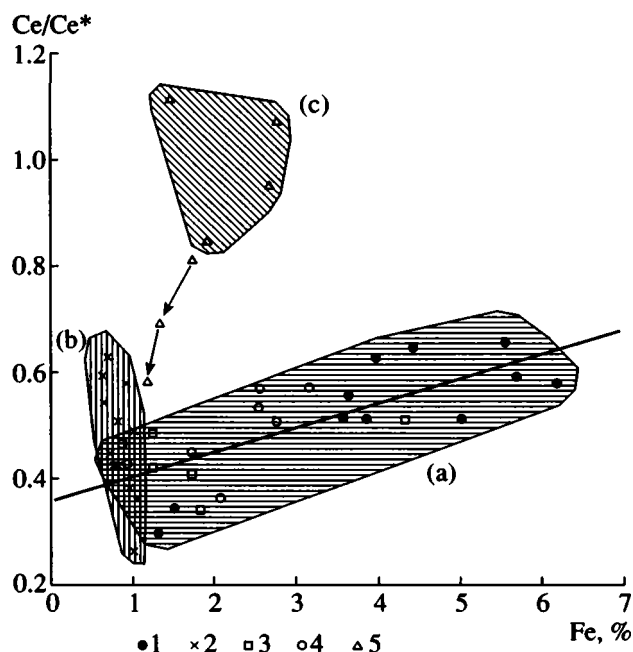


Fig. 7. Ce anomaly vs. Fe in Guatemala Basin nodules. Compositional domains: (a) upper sections and bulk samples of nodules, (b) lower sections of nodules, (c) micronodules. Arrows show compositional variations in micronodules from Station 3874 with respect to dimension. For other legends, see Fig. 6.

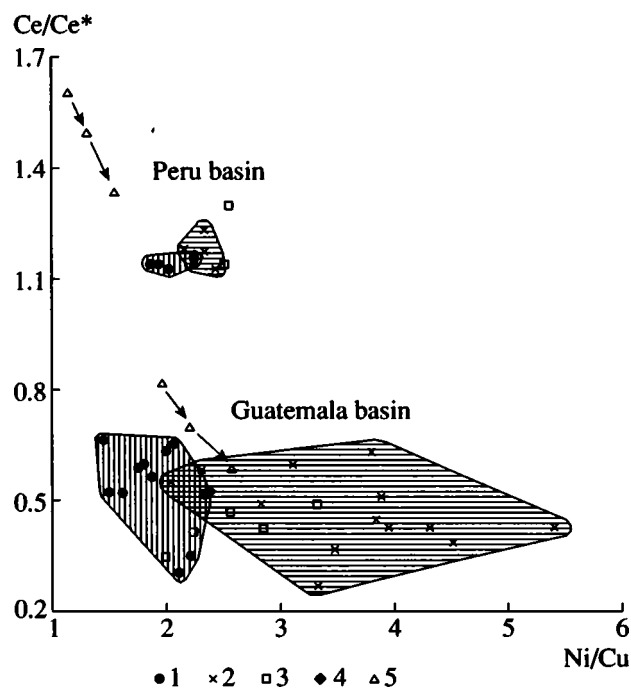


Fig. 8. Ce anomaly vs. Ni/Cu in nodules from Guatemala and Peru basins. (1) Upper sections of nodules; (2) lower sections of nodules; (3) bulk samples of nodules (Dymond *et al.*, 1984; Dubinin and Strekopytov, 1994); (4) nodules (Station 3874); (5) micronodules. Arrows show compositional variations in micronodules with respect to dimension.

At Station 56 in the Peru Basin, we can observe a mimicry of regularities observed at Station 3874. Results of the study of sediments from Station 56 have been reported in several works (Dubinin and Volkov, 1986, 1992; Dubinin and Strekopytov, 1994). The latter work described compositions of six nodules from a single grab sample. The upper and lower sections of nodules were analyzed in four nodules. The P-Fe correlation is clearly seen in micronodules and host sediments (Fig. 9). The REE distribution in nodules correlates with iron oxyhydroxides and P (Fig. 3). In contrast to other REE, the Ce concentration in sediments is governed by reactive iron oxyhydroxides. Sediments are more enriched in REE (III) than one could expect from the assumption of the sole contribution of iron oxyhydroxides. Based on the modulus value of $Al/(Al + Mn + Fe) < 0.4$ (Boström, 1973), sediments from Station 56 cannot be assigned to the hydrothermal type. However, we have registered a negative Ce anomaly that is similar to the anomaly at Station 3874 and is typical of hydrothermal sediments in oceans.

The P-Fe correlation in nodules and reactive sediments from Station 56 (Fig. 9) can be expressed by the linear regression $[P] + 0.010[Fe] + 0.097$ ($n = 11$). In nodules from the radiolarian belt of the equatorial zone, this correlation is expressed by the equation $[P] = 0.010[Fe] + 0.125$ ($n = 104$) (Dubinin *et al.*, 1997). It is well seen that these linear regressions have a similar

slope. The free member, which is the only distinctive parameter, suggests a higher amount of bone detritus in pelagic conditions of the radiolarian zone. In contrast, sediments from Station 56 were accumulated in mioepelagic conditions with a higher bioproductivity of water (Vinogradov *et al.*, 1996). The common Fe-P-REE(III) correlation indicates that REE(III) in sediments here are significantly associated with iron oxyhydroxides containing phosphate groups (iron hydroxophosphates).

Iron hydroxophosphates can be obtained during the sorption of dissolved phosphate from oceanic water by iron oxyhydroxides. At Station 56, in contrast to Station 3874, sediments were accumulated in deeper pelagic conditions; therefore, the Ce concentration in nodules here is higher; however, the C_{org} concentration is lower; and the intensity of suboxidative diagenesis is also apparently weaker (Table 1). Reactive sediments from both stations are compositionally closer to macronodules rather than micronodules. Micronodules are marked by the higher Ce anomaly and Mn/Fe values. In coarser fractions of micronodules, the Ni/Cu ratio increases and approaches the values that are typical of lower sections of nodules (Fig. 8), suggesting a stronger role of reductive diagenesis in the Mn component of ferromanganese aggregates.

The mass distribution between micronodule fractions in sediments is specific (Table 1). At stations 3874

and 56, the 250–500 μm fraction is maximal, while the 50–250 μm fraction prevails at Station 3834 (horizons 55–57 and 65–67 cm). The correlation of micronodule concentration with fraction size is inverse at the lower (65–67 cm) horizon. However, this trend is disturbed at the upper (55–57 cm) horizon as a result of the increase of the >500 μm fraction containing dendritic micronodules that are morphologically different from finer fractions. The Mn/Fe ratio growth in micronodules is a consequence of the intensification of suboxidative diagenesis. Based on the correlation between Ce–Fe and REE(III)–P systems in host sediments and micronodules (Fig. 5), one can infer that the material for micronodules was supplied by reactive sediments. The presence of hiatus at 55 cm (Sval'nov, 1991; Sval'nov *et al.*, 1991a) indicates that the diagenetic redistribution of material was intensified as a result of the delivery of additional organic matter. High concentrations of the hydrothermal Mn (as much as 14%) could result in its partial reduction after the washout of sediments containing organic matter or benthic organisms. The interference of the near-surface oceanic layer, which is currently characterized by a high bioproductivity (Romankevich, 1977; Vinogradov *et al.*, 1996), could produce more diagenetic micronodules in the surface (55–57 cm) layer, modify the relationship between fractions, and increase the Mn/Fe value (Tables 4, 5). The low organic content in sediments from the 56–62-cm horizon (Table 1) could be provoked by the high Mn concentration and MnO_2 formation.

The data on REE distribution in different micronodule fractions demonstrate that the Ce anomaly inversely correlates with fraction dimension and material supply. Diagenetic processes result in the compositional leveling of micronodules and host sediments. Since the REE distribution in nodules are always associated with iron oxyhydroxides and hydroxophosphates, the change of phase interrelations induces the change of REE distribution as well.

The positive Ce anomaly in hydrogenic oxyhydroxides mirrors the process of Ce oxidation in surficial waters of ocean and the accumulation of Ce in suspension below the oxygen minimum zone (Masuzawa and Koyama, 1989; Bertram and Elderfield, 1993; Sholkovitz *et al.*, 1994). The phase analysis and mineralogical examination of hydrogenic crusts revealed intricate aggregates of ferromanganese oxyhydroxides (Uspenskaya and Skornyakova, 1991; Koschinsky and Halbach, 1995; Dubinin, 1998). However, the sorption of phosphate-ion from oceanic water by ferromanganese oxyhydroxides is strongly limited. Based on experimental data, manganese oxyhydroxide can extract <10% P contained in the 0.1M KCl solution at pH = 7.5–8.0. The sorptional capacity of iron oxyhydroxide in respective conditions equals to ~95% P (Balistreri and Chao, 1990). Hence, manganese oxyhydroxide will inhibit the phosphate sorption by iron oxyhydroxide in compound ferromanganese oxyhydroxides that are typical for hydrogenic (sedimentational) oceanic sedi-

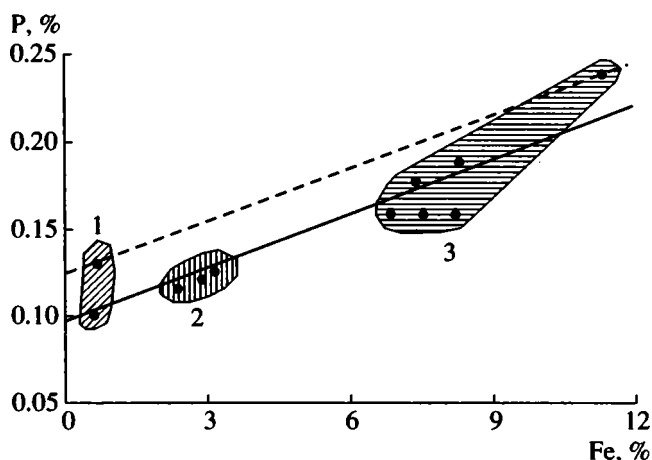


Fig. 9. P vs. Fe in reactive sediments from Station 56, Peru Basin. (1) Sediments; (2) micronodules; (3) upper and lower sections of nodules (Dubinin and Strekopytov, 1994). The solid line depicts the P–Fe regression equation for sediments from Station 56: $[P] = 0.010[Fe] + 0.097$. The dotted line shows the P–Fe correlation in nodules from the equatorial Pacific: $[P] = 0.010[Fe] + 0.125$ ($n = 104$) (Dubinin *et al.*, 1997).

ments with intricate aggregates of ferromanganese oxyhydroxides.

If the diagenetic reduction of Mn commences in suspension (Sholkovitz *et al.*, 1994), iron oxyhydroxides can absorb phosphate-ion from oceanic water. Iron hydroxophosphates, which are formed during this process, fit the chemical formula $\text{Ca}_2\text{FePO}_4(\text{OH})_4$; i. e., they include Fe, P, and Ca. Like bone detritus, they extract REE from benthic waters but are depleted in Ce (Dubinin and Strekopytov, 1994; Dubinin and Sval'nov, 1997). Iron hydroxophosphates are generated by the suboxidative diagenesis of sediments during the submarine discharge from hydrothermal sources and weathering of the volcanoclastic material (Dubinin *et al.*, 1997; Dubinin and Sval'nov, 1997; Dubinin, 1998). The introduction of iron hydroxophosphates into nodules decreases the positive Ce anomaly, since the REE(III) concentration is increased. In oceanic regions with an elevated bioproductivity of surficial water, fine micronodules are formed at the water–seafloor interface. Their suboxidative diagenesis is minimal, and the positive Ce anomaly is maximal. Ferromanganese nodules are developed during different (in time and intensity) phases of the suboxidative diagenesis of the sedimentary material. The contribution of reactive sediments grows with increasing micronodule dimension and attains maximal values in macronodules.

CONCLUSION

The REE distribution pattern suggests that the hydrogenic feature is more impressive in micronodules, relative to nodules in regions with a strong impact of hydrothermal processes and higher bioproductivity

of surficial water. The interference of suboxidative diagenesis is minimal in fine micronodules that are developed at the water-seafloor interface. The inverse correlation between the Ce anomaly and dimension of ferromanganese nodules is related to the influence of iron hydroxophosphates as a result of the sorption of dissolved phosphate-ion by iron oxyhydroxide in the absence of the close connection between manganese oxyhydroxide and dissolved phosphate-ion. The REE sorption on phosphate surfaces of iron oxyhydroxide from the water mass provokes a Ce deficit in nodules. Interrelations between micro- and macronodules suggest that the micronodule generation can represent the initial stage of nodule formation in oceans.

ACKNOWLEDGMENTS

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Some Features of the Evolution of Carbonate Accumulation in the Earth's History: Communication 1. Evolution of the Intensity, Mechanism, and Setting of Carbonate Accumulation

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Abstract—Marine and oceanic carbonate accumulation during the Vendian–Cambrian was mostly controlled by the life activity of organisms, which either constructed skeletons and directly transferred carbonates into sediments or created geochemical environments favorable for the precipitation of the carbonate substance. During the first third of the Paleozoic, the chemogenic and biochemogenic mechanisms of limestone formation were replaced by the biogenic one. In the dolomite formation, to the contrary, the chemogenic mechanism progressively replaced the biochemogenic mechanism and its pseudobiogenic modification. The carbonate accumulation occurred in the cyclic mode and its intensity increased with time to reach its peak in the Late Cretaceous. The main paleogeographic domains of carbonate accumulation also experienced changes. They were mainly represented by spacious shelf seas in the Paleozoic; by intraoceanic shoals, reefs and pelagic realm in the Mesozoic; and by the pelagic realm and, to a lesser extent, reefs in the main Cenozoic.

Carbonate deposits likely represent the first or one of the first objects, which allowed the evolution of sedimentary rock formation in the Earth's history to be traced. As early as the beginning of the current century, Daly (1909) established that, during the Paleozoic to Cenozoic, the dolomite abundance sharply decreased and was simultaneously replaced by limestone. Later, this trend was confirmed by Vinogradov *et al.* (1952) based on the numerous data from the Upper Precambrian and Phanerozoic section of the East European Platform. Chilingar (1956) arrived at the same conclusion.

In his fundamental monograph dedicated to limestone–dolomite facies of modern and ancient basins, Strakhov (1951) showed that the general "...facial profile of (ancient–V. K.) carbonate rocks is characterized by the same main features as today" (p. 288). Nonetheless, these are features of the evolution of carbonate accumulation, for instance, suppression of "...chemical calcite formation by the biogenic one" and "...disappearance of primary dolomites and formation of only their diagenetic (in wide and narrow sense) varieties" (*ibid.*, p. 356). Strakhov also substantially specified a periodicity, which was previously noted by Pustovalov (1940), in the carbonate accumulation in the Earth's history.

Extremely abundant quantitative data on the carbonate accumulation representing one of the most important domains of the sedimentary rock formation, in general, were obtained by Ronov (1980, 1993), who also formulated the *main law of carbonate accumulation*.

The significance of Ronov's work is not only in its conclusions, but also in the collected and systematized material, which can serve as a basis for the further analysis of different aspects of carbonate formation.

Problems of evolution of carbonate accumulation were also discussed in the modern foreign publications (*Sedimentary environments...*, 1996; Tucker and Wright, 1990; Wilson, 1980).

Abundant data on carbonate deposits obtained throughout the world during the last 20–30 years allows one to consider many aspects of the evolution of carbonate accumulation in the Earth's history, to revise previously established facts and concepts, to specify the latter, and to solve some problems as well as to pose new ones.

This work considers the Phanerozoic and, only partly, Late Precambrian–Vendian history of exclusively marine carbonate accumulation, which is generally responsible for the formation of most carbonate rocks. Considering the problem of the evolution of carbonate accumulation, one touches some previously established regularities and uses data obtained earlier. Specifically, the work adopts geochronological scale and data obtained earlier by Ronov (1993).

GENERAL TRENDS IN THE CARBONATE ROCK DISTRIBUTION IN THE STRATOSPHERE

Along with clayey and detrital varieties, carbonate rocks form a triad of the most important and widespread rocks of the Earth's sedimentary cover. Accord-

ing to empirical data of different researchers, the content of carbonate rocks varies from 18 to 29 vol % of sedimentary rocks (Ronov *et al.*, 1990; Ronov, 1993). According to Ronov (1993), they make up 20.4 vol % of Neogene sedimentary rocks. This value is close to that of detrital rocks (25.0%). Thus, the total volume of carbonate rocks is $200.6 \times 10^6 \text{ km}^3$.

According to Ronov, the relative content of carbonate rocks successively increases from continents to shelf areas, continental slopes, and oceanic bottom (17.8, 20.7, and 35.1 vol %, respectively). The absolute volume of these rocks decreases in the same direction, from 118.6 to 43.1 and $39.0 \times 10^6 \text{ km}^3$, respectively (calculations are based on the data from Table 5 of the cited work). The relation of absolute volumes of these rocks between modern continental and oceanic segments of the stratisphere is somewhat unexpected. Oceanic sediments are known to exist since the Late Jurassic and they are generally characterized by low thickness; nevertheless, their volume is only four times lower than the volume of deposits of the continental segment (continent + shelf + continental slope), where they are distributed throughout the entire Neogene.

These values characterize the modern structure and cannot be used for the analysis of the evolution of carbonate accumulation because the recent continental block includes deposits of ancient continents (in fact, platforms) and ancient oceans. Unfortunately, Ronov did not cite such data for the separate age intervals. It is possible that this is related to his rejection of ideas of new global tectonics and lithosphere plate drift. This fact is clearly indicated in his note to the description of the Vendian palinspastic reconstruction in the atlas of the lithological-paleogeographic world maps (Ronov *et al.*, 1984, p. 50).

As a general qualitative estimate, the volumes of carbonate deposits on platforms and in geosyncline structures can be calculated; the latter were mainly formed on the oceanic crust or at least in the marginal parts of oceans. Significantly more difficult are calculations in orogenic domains, which appeared as a result of both the closure of geosynclines and collision of continental blocks. Fortunately, volumes of carbonate rocks in orogens are generally insignificant and they can be neglected when defining general trends of evolution.

Taking into consideration the aforesaid information, data of Table 20 from the cited Ronov's work were accordingly recalculated. It was established that the relative content of carbonate rocks decreases from the Paleozoic to Mesozoic and Cenozoic (34.8, 26.1, and 19.8%, respectively) in platforms and increases (8.2, 17.9, and 20.6%, respectively) in geosynclines. The content of these rocks in orogenic domains varies from 0.8 to 8%. In the absolute volumes, carbonate deposits in Paleozoic platform domains are almost twice higher than those in geosynclines, which are arbitrarily considered, as noted above, to have an oceanic origin

(32.2×10^6 and $16.5 \times 10^6 \text{ km}^3$, respectively). In the Mesozoic, the volume of geosynclinal carbonates slightly exceeds that of platform carbonates (19.7×10^6 and $18.9 \times 10^6 \text{ km}^3$, respectively), whereas in the Cenozoic, the volume of platform carbonate deposits is virtually equal to that in geosynclines (3.7×10^6 and $3.4 \times 10^6 \text{ km}^3$, respectively). If these values are added by volumes of the Upper Jurassic-Pliocene oceanic carbonate deposits, then it appears that volumes of the Mesozoic and Cenozoic oceanic carbonate deposits significantly exceed volumes of these rocks developed in the continental segment.

All of these calculations are quite arbitrary and are based on significant assumptions. Nevertheless, the tendency of the shift of carbonate accumulation to the oceans probably exists, and the causes of this phenomenon will be considered below.

In order to study the distribution of carbonate deposits throughout the section, only data on the modern continental block (data from Table 20) were used; this allows the comparable, although qualitative results to be obtained.

The volume of the Vendian-Phanerozoic carbonate deposits amounts to $102.85 \times 10^6 \text{ km}^3$. Significant volumes of carbonate rocks are enclosed in all stratigraphic units (considered are stratigraphic units of a series rank), however, the irregular distribution patterns of carbonate accumulation that was established earlier is clearly preserved. For instance, the relative content of carbonate rocks within the series of the standard stratigraphic scale varies by more than one order, from 1.8% in the Pliocene to 26.3% in the Upper Cambrian. Provided that extremely low values characteristic of the Pliocene are excluded, the amplitude of variations becomes four times less (6.5% in the Oligocene versus 26.3% in the Upper Cambrian). If the content of carbonate rocks within the particular stratigraphic interval relative to their total amount in the Vendian-Phanerozoic is analyzed, then the scatter of values appears to be significantly higher, from 0.17% in the Pliocene to 9.8% in the Upper Cretaceous. The sharp difference is retained even if the extremely low contents in the Pliocene are excluded, 1.12% in the Paleocene versus 9.8% in the Upper Cretaceous. The intensity of carbonate accumulation, i.e., an amount of the carbonate material deposited in the time unit differs approximately by an order from 35.57×10^3 and $46.29 \times 10^3 \text{ km}^3/\text{Ma}$ in the Vendian and Pliocene, respectively to 323.60×10^3 , 358.12×10^3 , and $381.36 \times 10^3 \text{ km}^3/\text{Ma}$ in the Late Cretaceous, Late Devonian, and Early Triassic, respectively. Though being objective at first sight, the intensity is generally not very representative because it depends, to a significant extent, on the duration of the corresponding period; maximum values correspond to the short period of the Early Triassic (5 Ma), and only in the Late Cretaceous (31.1 Ma long), the high carbonate accumulation rate provides an accumulation of great amounts of carbonate rocks com-

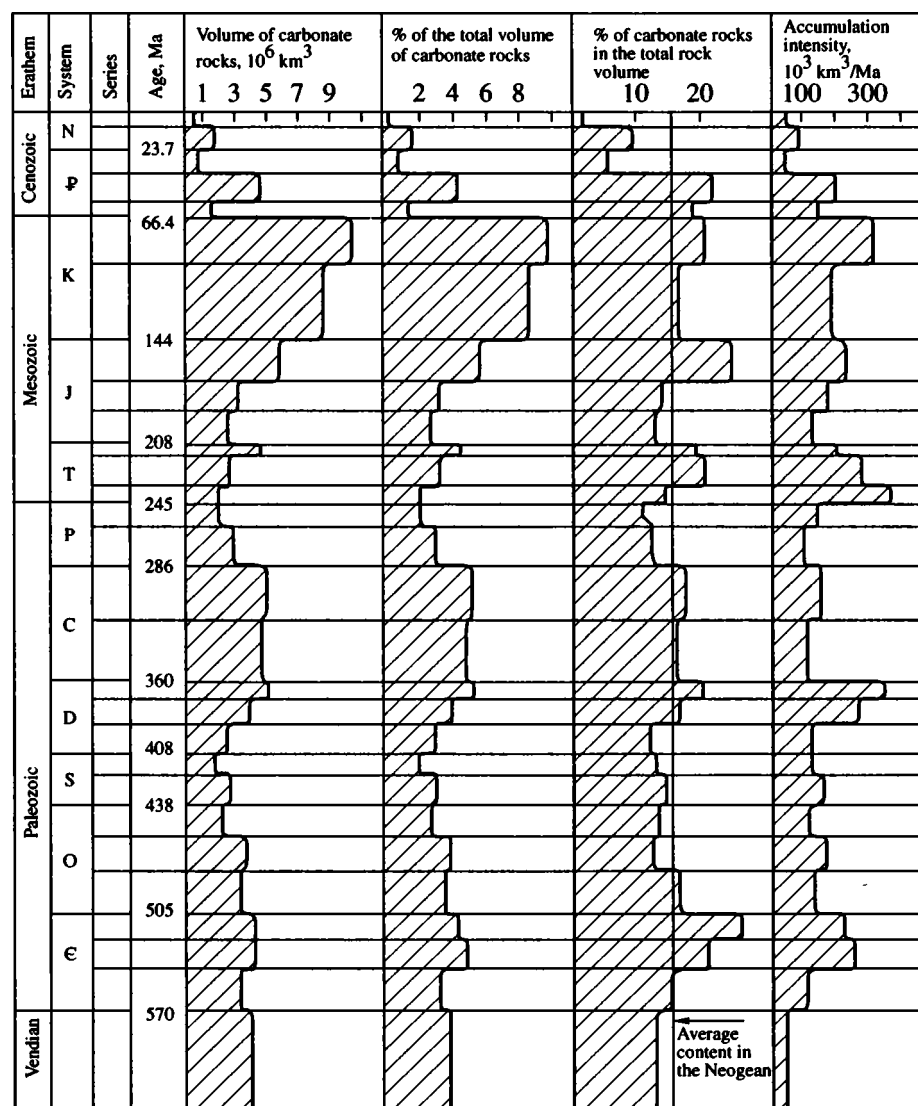


Fig. 1. Evolution of carbonate accumulation scale in the Earth's history.

posing the tenth fraction of all Vendian–Phanerozoic carbonate rocks.

Variations in the absolute volumes of carbonate rocks are less significant (from 171.29×10^3 and 622.64×10^3 km³ in the Pliocene and Oligocene, respectively, to 8492.73×10^3 and 10063.83×10^3 km³ in the Early and Late Cretaceous, respectively). Based on the volume of carbonate rocks, at least three large peaks (Middle Cambrian–Middle Ordovician, Middle Devonian–Carboniferous, and Late Jurassic–Cretaceous) and also two relatively small peaks (Late Triassic and Eocene) were established. Volumes of carbonate rocks corresponding to these peaks progressively increase with time and are equal to 15.86×10^3 , 18.49×10^3 , and 24.10×10^3 km³, or 15.42, 17.98, and 23.43%, respectively, which make up to 56.83 vol % of Ven-

dian–Phanerozoic carbonate rocks. These peaks are generally manifested also in other parameters.

Data on the quantitative distribution of carbonate rocks within the geological section are graphically presented in Fig. 1. The characteristics of carbonate accumulation is represented by four parameters: the absolute volume of carbonate rocks corresponding to the stratigraphic scale units, the proportion of carbonate rocks in the total rock volume of the specific stratigraphic units, the proportion of carbonate rocks in the specific stratigraphic unit in the total Vendian–Phanerozoic carbonate rocks, and the intensity of carbonate accumulation (the scale of U.B. Harland, with co-authors accepted by Ronov with some corrections for the Cenozoic, was used to characterize the duration of periods).

EVOLUTION OF MECHANISMS OF CARBONATE SUBSTANCE PRECIPITATION

Before considering the evolution of carbonate precipitation mechanisms, it is necessary to dwell on the mechanisms of its precipitation. All were described sufficiently long ago, but their critical analysis allowed the role of particular mechanisms to be specified and correctly understood and their significance to be quantitatively estimated because, despite the fact that they are well known, the impact of tradition is often very strong, distorts the situation, and retains the priority of earlier views.

Three mechanisms of carbonate precipitation are recently known as biogenic, biochemogenic, and chemogenic.

From the viewpoint of recognition in the field, the simplest mechanism is represented by the biogenic one; organisms extract calcium carbonate and, less commonly, magnesium carbonate from sea water to build their skeletons using carbonate minerals (commonly calcite, aragonite or high-Mg calcite, and, very rarely, other carbonate minerals). There are numerous invertebrate types and classes amid such organisms: foraminifers, brachiopods, various mollusks, corals, stromatopores, echinoderms, bryozoans, and others.

The biochemogenic mechanism is related to the vital activity of algae and cyanobacteria, which use carbonic acid dissolved in water during the photosynthesis. Thus, changing the geochemical environs, first of all the pH value, form conditions favorable for carbonate precipitation. Two variants are possible during this process. In the first case, environmental changes are local and occur directly in organisms (or their colonies), and they result in calcification of certain parts of algae or algal (cyanobacterial) mat. The classic examples of such structures are stromatolites, many microbial structures (films, crusts, nodules), and also groups of Cyanophyceae algae, which were termed calcibionts (*Epiphyton*, *Girvanella*, *Renalcis*, and others) by Luchinina (1988, 1990). Morphological peculiarities allow their formation to be related to the vital activity of organisms, i.e., to consider the mechanism of their formation as arbitrarily biogenic or pseudobiogenic.

In the second case, environmental changes occur over large areas of the basin, and the carbonate material precipitates from water, where it forms suspension (minute crystals). As a result, usual pelitomorphic and micrograined carbonate mud is formed. This process can be exemplified, for instance, by the formation of the carbonate material in the form of whitish spots in the Red Sea and Persian Gulf related to the seasonal phytoplankton bloom (Wells and Illing, 1964), and by precipitation of calcareous-magnesian compounds including protodolomite in the Coorong Lagoon in Australia. It should be noted that the Red Sea is characterized by slightly elevated salinity (to 4.2%) as compared with the average oceanic one, whereas in the Coorong Lagoon, carbonate precipitation occurs under lowered

salinity but under the elevated pH value that amounts to 8.2–8.4 in periods of the intense vegetation development (Von der Borch and Lock, 1979).

In order to recognize and substantiate the purely chemogenic precipitation of the carbonate material is significantly more a difficult task. Presently, it is common to exclude all the crystalline varieties from this group of rocks, which were previously often considered as having the chemogenic origin, but, in fact, are formed as a result of secondary recrystallization of different-origin rocks or due to metasomatic dolomitization of limestone. Therefore, chemogenic rocks include only pelitomorphic and oolitic limestones.

Nonetheless, the chemogenic origin of the latter rocks is debatable. For instance, their study using a sophisticated equipment instead of the traditional polarization microscope revealed that many pelitomorphic carbonate rocks are of biogenic origin. The most characteristic example are the Upper Cretaceous pelitomorphic limestones from the Tethys. Previous views that they represent chemogenic rocks appeared to be erroneous because their study using the scanning electron microscope showed that they enclose abundant coccolithophorid fragments; i.e., they represent a compact chalk. Another example was provided by recent micrograined sediments of the Black Sea, which appeared to consist mostly of coccoliths (Bakri *et al.*, 1970; Trimonis, 1973). Electron-microscopic studies of recent mud from the Great Bahama Bank showed that spicular aragonite crystals in pelitomorphic sediments largely represent a product of destruction of calcareous algae, foraminifers, mollusks, and corals (Stieglitz, 1972). In the Aqaba Bay, most of micritic particles are also formed at the expense of destroyed algae (Friedman *et al.*, 1973). In some cases, micritic and peloidal limestones represent a product of cyanobacteria vital activity (Kazmierczak *et al.*, 1996). Finally, many pelitomorphic and micrograined muds are formed by the biochemical way.

Similarly ambiguous is the interpretation of oolites as rocks of the purely chemogenic origin.

First, there are many transitions between oncolites formed by Cyanophyceae algae and "pure" oolites, and no distinct boundary exists between "true chemogenic oolites" and biochemogenic (pseudobiogenic) oncolites, which casts some doubt upon the purely chemogenic origin of the latter. Paleontologists determine many of these "oncolites" as microphytolites discriminating particular groups such as *Osagia*, *Asterosphaeroides*, *Radiosus*, *Vermiculites*, and others among them. Second, the study of oolites from the Great Bahama Bank, Persian Gulf, and other areas of the recent carbonate formation revealed that the concentric structure of oolites is related to intercalation of spicular aragonite crystals located in the tangential mode and organic matter, algal mucus (Patrunov, 1976). Third, Sr concentrations in modern oolites are higher as compared with those which, according to thermodynamic

calculations, could exist under the actual temperature and pressure in aragonite (in the form of the isostructural strontianite admixture). An excessive (by 14–15%) amount of Sr is explained by bacterial and algal vital activity (Kinsman, 1969). The formation mechanisms of ooidal structures were considered in detail earlier (Radionova, 1976).

When discussing the problem of chemical carbonate precipitation, it is necessary to consider the data of the sea water chemistry (Alekin and Lyakhin, 1968, 1984). In tropical areas, it was established that calcite dissolution in surface waters is 7–8 times higher as compared with its average value. Experiments revealed that spontaneous purely chemical calcium carbonate precipitation from sea water requires 50-fold oversaturation of solution, which is unattainable under natural conditions. Nonetheless, chemogenic precipitation of minerals occurs on the long-term scale, but sizes of formed crystals are close to colloidal and they are present only in the suspension. Their precipitation is possible only by two ways. First, they are used by filter feeders, which transmit large volumes of water through their bodies and inhibit dispersed particles of calcium carbonate, which dissipate into small lumps and aggregates and then they precipitate. Second, the carbonate material precipitates on the available larger crystals that serve as inoculation: shell detritus, particles suspended in littoral waters, and others. It is easy to see that both these mechanisms increase the volume of carbonate substance by chemical precipitation with noticeable, although indirect, participation of organisms.

The aforesaid does not concern the crystalline cement, the crystalline carbonates in stromatolites, the structures of the "bird's eye" type, and others, which are largely diagenetic in origin and can compose the significant part of the rock but do not determine its origin.

Thus, within the scale of the chemical precipitation of carbonates, in particular, calcium carbonates appear to be sharply limited, and precipitation is controlled by the pH value that depends on the algal and bacterial vital activity rather than by the salinity and carbonate concentration in the water. Nevertheless, such a mechanism cannot be completely excluded; one should admit only its significantly limited scale, although in particular facies, the role of the latter can be important.

At first sight, it is incorrect to interpolate data from the mechanism of the modern carbonate precipitation on this process in geological history. Nonetheless, geological data suggest that precipitation processes, similar to the modern ones and whose signs are present in sedimentary sequences, occurred also in past epochs. Furthermore, the role and scale of different processes varied with time; moreover, they changed in a more complex way and probably were different during limestone and dolomite precipitation (Fig. 2).

In the total Vendian carbonate accumulation, calcium carbonate precipitation was apparently insignifi-

cant; its role sharply increased in the Cambrian, when pseudobiogenic and biochemogenic carbonate deposition probably prevailed. This is evident from the thick sequences of stromatolite limestone composed of calcibiont remnants: *Epiphyton*, *Renalcis*, *Girvanella*, and others. Chemogenic precipitation was probably significant as well.

These precipitation mechanisms functioned also during the entire Phanerozoic history, but their quantitative significance was sharply reduced. According to Luchinina (1990), calcibionts and Cyanophyceae algae were generally widespread in the Vendian and Paleozoic (particularly, the Early Paleozoic). Their abundance significantly decreased in the Mesozoic and they dwelt only in fresh-water basins in the Cenozoic. According to an assumption (which is also confirmed by geological data) that after its intense development in the Early Paleozoic, pseudobiogenic precipitation of carbonates could progressively decrease in the stepwise mode. The precipitation in the form of stromatolites was widespread in the Mesozoic and exclusive in the Cenozoic.

Since the second half of the Ordovician, the process of Ca extraction by organisms and its accumulation in the form of carbonate sediments rapidly increased. In the mid-Paleozoic, this biogenic mechanism of carbonate accumulation became completely preponderant. Nevertheless, the type of biogenic carbonate accumulation was not unchangeable. In the Paleozoic, preponderant was probably the formation of limestones at the expense of the vital activity of benthic organisms, amid the important rock-forming role belonging to Stromatoporoidea, Tabulata, Rugosa, Brachiopoda, Foraminifera, Crinoidea, Bryozoa, and algae (mainly Cyanophyceae). In the Mesozoic, benthogene accumulation of limestones continued, but its scale reduced. To a certain extent, the composition of Ca-producing organisms also changed. For instance, the role of benthic foraminifers and crinoids decreased, Coelenterata were dominated by hexacorals, algae were mainly represented by Rhodophyceae forms, and brachiopods were largely replaced by mollusks.

The principal event was a new role of nektonic and planktonic organisms in particular, and a corresponding sharp increase in the development of carbonate formations accumulated at the expense of these organisms. This mechanism of carbonate precipitation first became noticeable in the Late Silurian, when *Orthoceras* limestones of the Carnic Alps were formed. In the Devonian–Earliest Carboniferous, it became widespread resulting in the formation of cephalopod, stiliolin, and tentaculite limestones. In the Triassic–Jurassic, these facies are represented by ammonite limestones (Upper Triassic of the Eastern Tethys, Jurassic ammonitico rosso facies in the Alpine zone, and others). This mechanism acquired a leading role in the Late Cretaceous when the major portion of calcium carbonates was used and precipitated by coccolithophorids; in the Cenozoic,

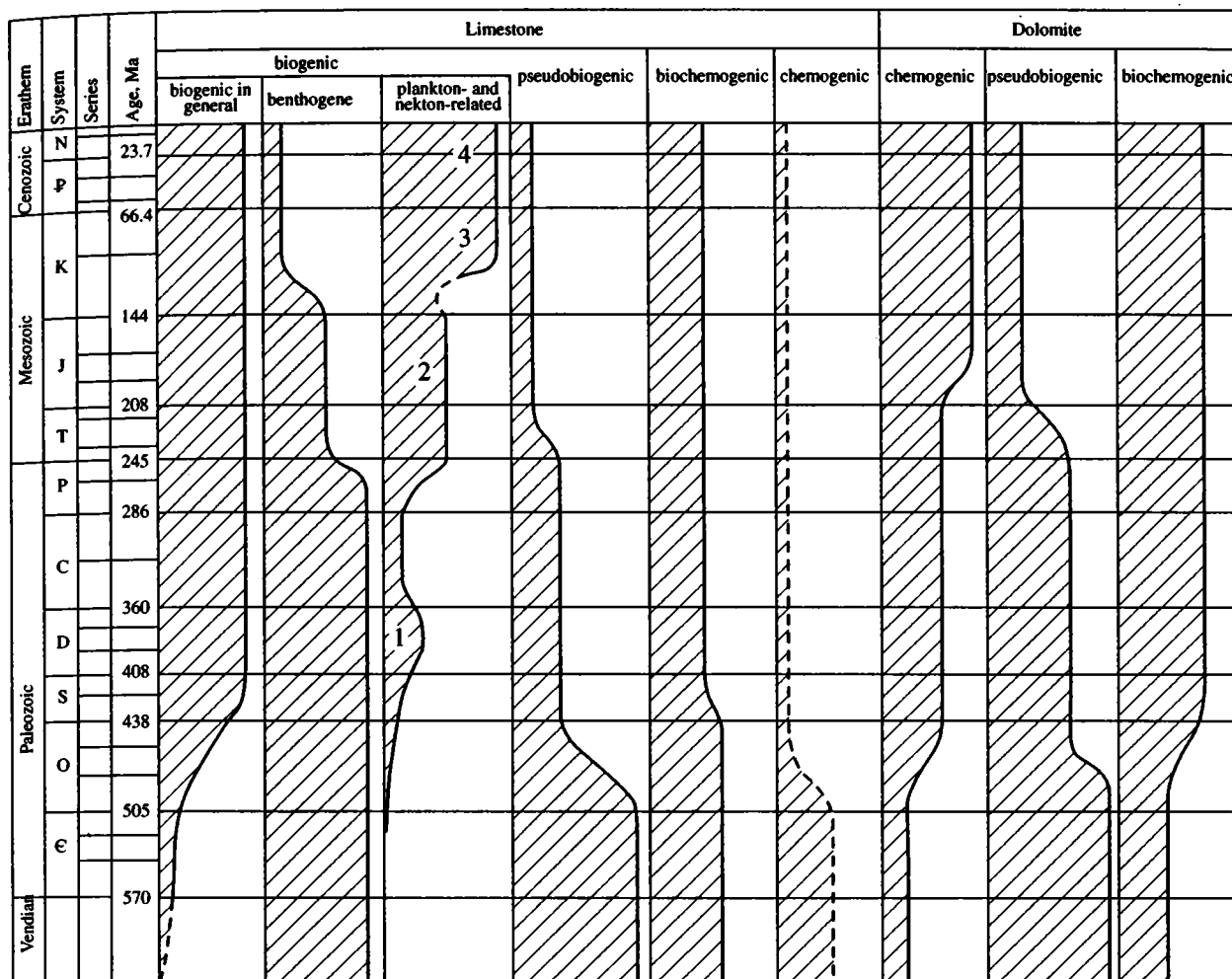


Fig. 2. The principal scheme demonstrating evolution of carbonate precipitation mechanisms. Main carbonate-producing organisms: (1) cephalopods, tentaculites, styliolinids; (2) ammonites, coccolithophorids; (3) coccolithophorids; (4) foraminifers, pteropods, coccolithophorids.

main carbonate-producing organisms were pteropods and planktonic foraminifers in particular.

A different precipitation mechanism was characteristic of dolomites. Despite the fact that the study of dolomite began more than two centuries ago, when D. Dolomie described this mineral, the problem of its formation is far from its solution. Moreover, the number of possible processes and settings, which are thought to be responsible for its formation, is constantly increasing. In many cases, these processes and conditions of dolomite formation are sufficiently well-studied and substantiated; views about its monogenic nature should become a history. It can be postulated with sufficient confidence that there are several mechanisms of its formation and that it can be accumulated in different settings. These problems are actively discussed in Russian and western publications (Bezborodova, 1988; *Concepts...*, 1980; *Dolomitization...*, 1965; Hardie, 1987; Patrunov, 1983; *Sedimentology and geochemistry...*, 1988; Tucker and Wright, 1990).

Leaving aside advantages and disadvantages of particular mechanisms as well as their quantitative role in dolomite accumulation, an attempt is undertaken to briefly follow their evolution in time. In doing so, one essential point should be noted. In most cases, petrographic data (morphology of crystals, their relationships, and others) indicate the secondary nature of dolomite, which is confirmed by its frequent development after primary rocks (sediments). Nonetheless, the sufficiently close relationship of dolomites with particular facies indicates that their formation is confined, despite the secondary nature, to certain settings. The aforesaid does not concern catagenetic metasomatic dolomites; their presence is reliably established in some cases (e.g., Kholodov, 1988), but they do not determine the total dolomite balance in sedimentary cover.

There is no clear answer to the question concerning the form of precipitation (dolomite, protodolomite, or separate calcium and magnesium compounds) of the

primary substance which subsequently coalesces and crystallizes to form dolomite. Coprecipitation of calcium and magnesium compounds and *diagenetic* formation of dolomite as a separate mineral probably is a general rule. Therefore, it is principally important to consider mechanisms and conditions of precipitation that are typical of magnesian compounds but not dolomite proper, although precipitation of dolomite or, at least, protodolomite is probably possible in some cases.

In the Vendian, Cambrian and, partly, Ordovician–Silurian, the most important mechanisms of dolomite formation were pseudobiogenic and biochemogenic. Thick sequences of Upper Precambrian and Cambrian stromatolite dolomites and even “primarily” dolomitic Cambrian archaeocyathan–cyanobacterial reefs are well known (Davydov, 1975; Khabarov, 1985; and others). Similar rocks are sufficiently abundant also in the Ordovician–Silurian. Some researchers (for instance, Davydov, 1975) suggest the possibility of primary dolomite formation, whereas others believe that the primary product was represented by magnesian compounds and dolomite was formed later during diagenesis (Gebelein and Hoffman, 1979). It is conceivable that purely chemogenic dolomite also accumulated in the Early Paleozoic, although the scale of this process was hardly significant.

In this connection, it is pertinent to reflect upon the conclusions of I.K. Korolyuk, a very serious and thorough researcher, which concerned the classic objects such as the Lower Cambrian carbonate formation of the Siberian Platform. She wrote: “...pelitomorphic and micrograined carbonate rocks are extremely rare and account for about 2% of the rocks studied. According to widely shared opinion, these rocks are chemogenic in the nature” (Korolyuk, 1956, p. 58). Although “the widely shared opinion” cannot be considered reliable criteria, petrographic characteristics cited in the work allow these dolomites (probably primary protolomites) to be considered as having a chemogenic nature. Principally, it is important to emphasize a limited abundance of chemogenic rocks.

An association of dolomites with sulfates is not a clear criterion of the chemogenic nature of carbonates, because cyanobacteria also dwell in waters with elevated salinity. Besides, these basins are marked by the biochemogenic and pseudobiogenic precipitation rather than (and not only) the chemogenic dolomite precipitation. Korolyuk noted the occurrence of cyanobacterial colonies (*Collenia*) in anhydrite–dolomitic and gypsum–dolomitic rocks.

The similar situation is also observed in modern hypersaline water basins of the arid zone. For instance, stromatolite dolomites occur in the Aqaba Bay of the Red Sea with the salinity of 14.48‰; it is remarkable that the elevated dolomite content is usually characteristic of stromatolite layers, which are enriched in organic matter (Friedman *et al.*, 1973).

Different data on the cyanobacteria development in water basins with very high salinity, their association with sulfate rocks and even the formation of anhydrite stromatolites were discussed during the 15th International Sedimentological Congress held in Alicante in 1998 (Peryt, 1998; Turchinov, 1998); there are also publications dedicated to this problem (Aref, 1998; Peryt, 1996; and others).

Beginning from the second half of the Paleozoic, dolomite formation progressively tends to be localized in particular facies. The pseudobiogenic mechanism is sharply reduced, and the chemogenic and biochemogenic precipitation of magnesian compounds distinctly prevails. Subsequently, the material is transformed into dolomite. The early diagenetic, virtually syndimentary dolomitization, was similar to the eogenetic dolomitization considered below.

PALEOGEOGRAPHIC TYPES OF BASINS WITH CARBONATE ACCUMULATION AND THEIR EVOLUTION

Carbonate rocks are formed in the wide range of settings, from subaerial to deep-water oceanic. There are also onland calcareous tuffs (travertines) and lacustrine calcareous– and calcareous–dolomitic sediments, however, an overwhelming majority of carbonate rocks are formed in seas and oceans. Marine basins are also very variable: deep-water open oceans and spacious shallow-water “shelf” seas, narrow elongated basins such as the modern Red Sea or the Dnieper–Donets–Pripyat depression in the Late Paleozoic, inner and marginal seas, open and semiclosed bays, and others.

In general, all modern geographic and paleogeographic domains of carbonate accumulation within these basins can be subdivided into four types: (1) marine and oceanic shelves including the so-called ramp valleys (Ahr, 1973; Burchette and Wright, 1992); (2) large isolated intrabasin (usually intraoceanic) shoals; (3) different reefs; and (4) pelagic realm. The present-day data on distribution of different-type carbonate rocks allow a conclusion that the relative significance of these areas, with respect to volumes of carbonate sediments therein, changed in the Earth’s geological history (Fig. 3).

In the Late Precambrian and Paleozoic, carbonate accumulation was related to spacious and usually very shallow-water “shelf” seas, which covered stable blocks of the continental stratisphere (ancient platforms). These were, for instance, the Vendian–Cambrian seas of the Siberian Platform and adjacent Alazeya zone, the Cambrian seas with carbonate sedimentation in the Chinese Platform and Iran region (the latter represented a shelf of the huge continent that included Africa and Arabian Peninsula), the Late Paleozoic basins of the East European Platform, the Paleozoic seas of the North American Platform, and others.

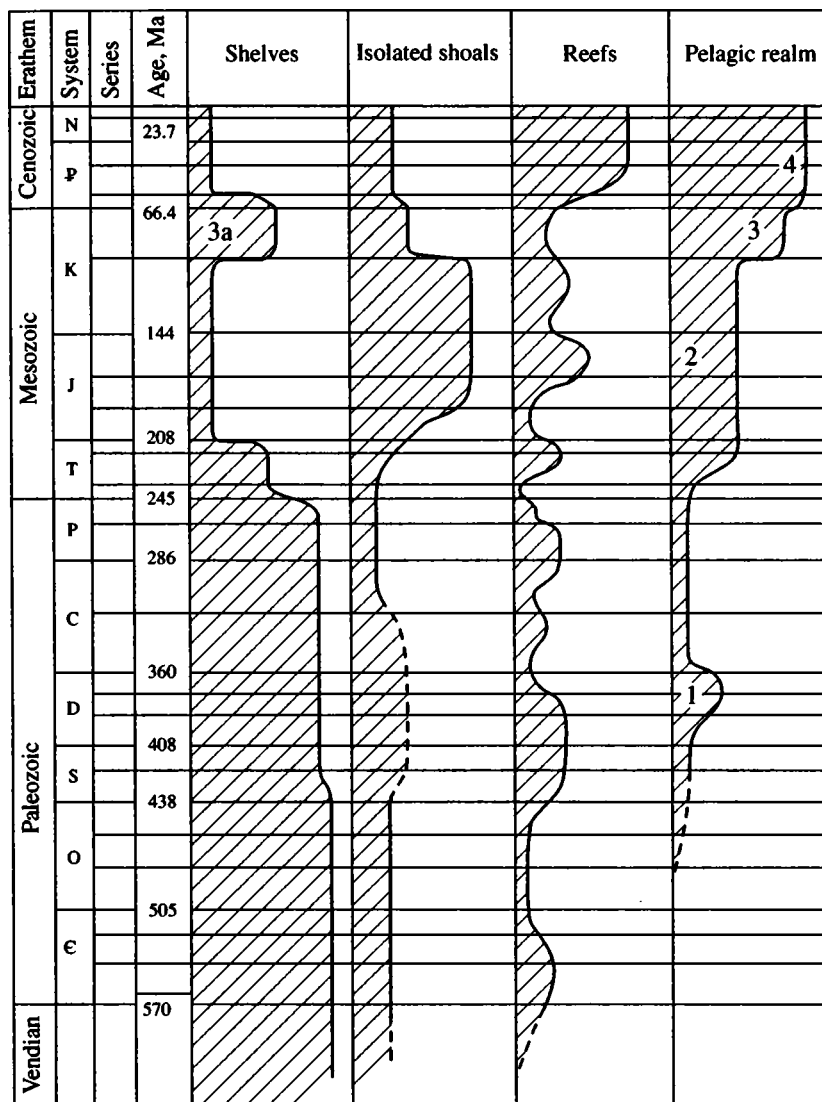


Fig. 3. Evolution of the relative role of different paleogeographic zones in carbonate accumulation. (1) Cephalopod, tentaculite, and styliolinitid limestones; (2) limestones of the ammonitico rosso facies, Maiolica, Hallstadt limestones, and others; (3) chalk formation; (3a) benthogene limestone and chalk on shelves; (4) nannofossil-pteropod-foraminifer limestone.

The dimensions of these seas were very large. For instance, the Late Devonian–Early Carboniferous basin of the East European Platform extended approximately from 32° to 60°E (in modern coordinates), i.e., over a distance at least 1800–1900 km from the west to the east, and from the northern Novaya Zemlya Archipelago (approximately 76°N) to the latitude at least south of Volgograd (47°N), i.e., over a distance of not less than 3000 km from the north southward. The Late Ordovician basin with carbonate sedimentation in North America extended from the modern Arctic islands of Canada to northern Mexico, i.e., over a distance of at least 8000–9000 km and a width of 2000–2500 km.

These platform seas were often characterized by the normal hydrological regime and oceanic salinity. They

were marked by the accumulation of benthogene carbonate formations with the abundant and diverse fauna. However, seas with the elevated salinity also existed, where evaporites accumulated along with carbonate sediments (Cambrian of the Siberian Platform, Silurian and Devonian of the North American Platform, and others).

Another paleogeographic type of the carbonate accumulation domain was represented by spacious shoals within ancient deep-water oceanic basins. They also accumulated benthogene carbonate and terrigenous-carbonate formations. Due to their morphology, these structures are termed isolated carbonate platforms in present-day publications, which are, for instance, the Famennian–Tournesian rocks of the Kazakhstan microcontinent, Upper Silurian–Lower

Carboniferous rocks of the Nyurol'ka and Khanty-Mansi structural-facial zones of West Siberia, Devonian rocks of the Altai and Salair regions, Frasnian rocks of the Golden Spike in Western Canada, Upper Permian (Zechstein) rocks of the Chartow platform in Poland, and others. All of them represented rigid blocks or microcontinents within the Paleosasiatic and Uralian paleoceans. Similar rocks are also recorded in other regions of the world.

Isolated carbonate platforms are characterized by steep slopes and bounded by deep-water facies along the entire periphery, unlike the epicontinental carbonate sequences, which are successively replaced by terrigenous coastal and continental rocks in one direction. In the opposite direction, they are gradually or abruptly replaced by various deep-water sediments and often fringed by reefs.

Dimensions of such shoals (isolated carbonate platforms) are variable. For instance, the Late Devonian-Bashkirian Astrakhan platform of the North Caspian microocean was approximately 150×175 km and accumulated the carbonate sequence about 2000 m thick (Kuznetsov, 1998). The Paleozoic Nyurol'ka carbonate platform buried under the Mesozoic-Cenozoic platformal sedimentary cover is about 10000 km² in size and characterized by the apparent thickness of carbonate rocks of about 3600 m; the Khanty-Mansi carbonate platform is approximately 20000 km². The Early-Middle Devonian Salair platform is approximately 350×500 km and accumulated about 4 km of carbonate rocks; the Famennian-Tourneisian Kazakhstan platform is 450×900 km and hosts the carbonate sequence of at least 2500 m thick.

The third domain of benthogene carbonate accumulation was represented by reefs. The latter developed within epicontinental seas (Cambrian of East Siberia, Silurian of the United States, Devonian of Canada, Lower Carboniferous of the East European Platform, and others) and on passive margins of continents often fringing platform carbonate rocks (Devonian and Permian of the Western Urals, Permian of the United States, and others). Intraoceanic reefs, and reefs fringing microcontinents and rigid blocks within oceans, are also abundant. The Paleozoic was marked by several epochs of the reef formation: Early-Middle Cambrian, Late Ordovician-Frasnian, Visean-Earliest Bashkirian, and Latest Carboniferous-Permian.

The purely pelagic precipitation of the carbonate material by nekton and plankton was probably on a sufficiently limited scale. The oldest example of such rocks are Upper Silurian *Orthoceras* limestones of the Carnic Alps, but their maximum development was in the Devonian-Earliest Carboniferous. Pelagic limestones of this age are recorded in the Rhine Shale Mountains, Harz, Turingia, Sudetes, Bohemia, Carnic Alps, Pyrenees, Cantabrians, Montagne Noire, the Bosphorus area, southeastern England, North Africa, Kazakhstan, Northern Pamir, Germany, and in other

regions. They are also described by M. Tucker, as well as in many articles dedicated to pelagic sediments (Bandel, 1974; Kuznetsov and Kurtze, 1985; Kuznetsov, 1987; *Pelagic...*, 1974; Rucholz, 1963; Tucker, 1973, 1974; Tucker and Kendal, 1973; Volodina, 1984; Voznesenskaya, 1979; Wald *et al.*, 1983; and others).

As a rule, these rocks are represented by: micrograined limestones, sometimes clayey; with a variable amount of fine organogenic detritus; with the thin-layered or, more frequently, flaser, lumpy structure with hardgrounds; and, often, with ferromanganese nodules. Fossils are distinctly prevailed by planktonic forms (cephalopods, conodonts, styliolinids, tentaculites); thin-shelled bivalves are present amid benthic remains. In the modern structure, these rocks compose a band, although it is conceivable that such patterns resulted from subduction and collisional processes. Commonly, they are characterized by their low thickness. For instance, there are sections in Harz, where Upper Devonian carbonate rocks are about 1 m thick (Rucholz, 1963). Therefore, the carbonate accumulation rate is estimated in most cases to be 2–3 mm/ka (Tucker and Kendal, 1963; Voznesenskaya, 1978), which is comparable with the accumulation rate of similar sediments in modern oceans.

It should be noted that most of the Paleozoic deep-water rocks known at present are represented by carbonate-clayey, clayey-siliceous, not purely carbonate varieties.

In the Mesozoic, four main types of carbonate accumulation domains discussed above were preserved, but the significance of each of them significantly changed. An abundance and, more importantly, dimensions of epicontinental platform shelf seas with carbonate sedimentation were reduced, which can be exemplified by relatively narrow shelves of the northern fringing of the Tethys: the Late Jurassic shelves of the Scythian and Turan plates, some shelves of the modern Mediterranean Sea including the Late Jurassic Dachstein shelf of the northern Calcareous Alps, the Early Jurassic Lessini shelf of the Trento platform in northern Italy, the Late Jurassic shelf framing the Iberian land, the Cretaceous shelf of Dinarides, and others (Bosellini, 1984, 1989; *Controls on Carbonate...*, 1989; Koch *et al.*, 1989; and others).

The substantially more intense carbonate accumulation was typical of intraoceanic shoals, where isolated carbonate platforms were formed. Their structure and evolution are studied within the Tethys, particularly in its Mediterranean part, and in the Western Atlantic (Bosellini, 1989; Foellmi, 1989). The opening of the Tethys and separation of lithospheric plates were accompanied by the appearance of abundant isolated blocks, which accumulated shallow-water benthogene carbonate sediments beginning from the Late Triassic-Early Jurassic. These are Triassic isolated Sella, Latemar, Sossolungo, Cernera platforms in the Dolomitic Alps, Late Jurassic Burgundia and Central plat-

forms in France, Friuli platform in northern Italy and Slovenien, and others.

The American Mediterranean of the Paleotlantic encloses the Middle Cretaceous Golden Line platform (Mexico) bounded by reefs and the Jurassic–Cretaceous Blake Plateau. Beginning at least from the Early Cretaceous or, according to geophysical data, Late Jurassic (Schlager and Ginsburg, 1981), the Bahamas Bank commenced to form; the latter is a classic example of an isolated carbonate platform, which generally represents a prototype of similar carbonate platforms. The total thickness of Mesozoic–Quaternary rocks covering this bank (the hole penetrated Upper Cretaceous rocks) exceeds 4860 m. In the southeastern Atlantic, Lower Cretaceous shallow-water benthogene carbonate deposits of the isolated carbonate platform are encountered by deep-sea drilling holes in the Walvis Ridge area.

The Late Triassic, Late Jurassic, Middle and, locally, Late Cretaceous were marked by an intense reef formation. Triassic–Jurassic reefs are registered virtually throughout the entire Tethys and along its margins. Middle Cretaceous rudist reefs were developed mostly in the Gulf of Mexico, Caribbean Sea, and along their peripheries; they were also distributed along western margins of Central Africa, northern framing of the Tethys, from Portugal via Turkey and Afghanistan to India, and Late Cretaceous buildups were recorded in North Africa and in the Middle East.

Similar to reefs are oceanic guyots, which are flat-top carbonate structures usually bounded by reefs and covered by pelagic sediments and presently subside to significant depths. Recently, they are often termed as seamounts. Unlike isolated carbonate platforms, oceanic guyots developed on volcanic edifices and are sufficiently well studied in the northwestern and central Pacific (Camoïn *et al.*, 1998; Groetsch *et al.*, 1993; Groetsch and Fluegel, 1992; Heezen *et al.*, 1973; Larson *et al.*, 1995; Shiba, 1993; Winterer and Sager, 1995; and others), which have the area of more than 2000 × 4000 km hosting more than 350 structures of such type. The thickness of carbonate deposits sometimes exceeds 1600 m and their age ranges at least from the Hauterivian to Albian. Shallow-water limestones contain abundant and diverse scleractinian, hydroid, echinoderm and various foraminiferal faunas, as well as Cyanophyceae algae, and other organisms. Such rocks were also described within the Tethys, particularly in Spain (Vera *et al.*, 1997).

The development of some isolated carbonate platforms, as well as carbonate shelves particularly along the northern European margin of Tethys, terminated in the Jurassic, when shallow-water carbonate sediments were overlain by deep-water limestones of the ammonitico rosso facies. However, most of these structures continued to evolve until the mid-Cretaceous and some of them until later epochs. At the end of the Early Cre-

taceous, the development of reefs and shallow-water carbonate deposits on guyots terminated.

A sudden and almost catastrophic termination of the carbonate platform, guyot, and reef formation in the middle Albian–Cenomanian and their overlapping by pelagic deep-water sediments is correlated with several important events: brief sealevel rise in the terminal Albian followed by its significant rise in the Turonian; cooling at the end of the Albian, although the Cretaceous was one of the warmest periods in the Earth's history (Frakes and Francis, 1988); the development of anoxic environments (Camoïn *et al.*, 1998; Schlager, 1992); and some others. It is hardly reasonable to directly relate termination of benthogene carbonate accumulation to the sealevel rise. The point is that the rate of biogenic precipitation of the carbonate material is sufficiently high and exceeds the sealevel rise (the eustatic- and, moreover, the subsidence-related). Dramatic events such as cooling, regressions related to the short-term sealevel falls, and, particularly, anoxic events could most likely cause the death of the carbonate-producing and reef-building fauna. The subsequent rapid sealevel rise resulted in the appearance of significant depths in these areas, which prohibited benthogene carbonate accumulation, and, thus, pelagic sediments began to accumulate. Rapid sealevel changes and cooling could cause the density stratification of the water column, which could result in anoxic environments. In other words, the evolution of carbonate platforms and reefs was most likely controlled by several factors.

It should be noted that the Albian–Cenomanian boundary period was not the only one in the Mesozoic, which was marked by termination of benthogene sedimentation, although it was one of the most important time intervals. There are hiatuses in benthogene carbonate accumulation related to the "anoxic event" at the Cenomanian–Turonian boundary, marked by pelagic sediments and followed by the reestablishment of shallow-water carbonate accumulation in the Turonian (Drzewiecki and Simo, 1997). Some Pacific guyots continued to evolve until the end of the Maastrichtian, Latest Eocene, and even until the present in the form of isolated carbonate platforms (the Bahama Bank), large atolls, and islands (Larson *et al.*, 1995).

The principal innovation in the Mesozoic was a sharply increased role of pelagic oceanic carbonate sediments. These are well-known Jurassic and Cretaceous ammonitico-rosso facies, Maiolica and Biancone formations of the Alpine zone and the western part of the Tethys, Triassic Hallstadt limestone and ammonite facies of its eastern part, particularly Timor Island, and others (Bosellini and Winterer, 1975; Clari and Martire, 1996; Jenkins, 1974; and others).

Rocks of the ammonitico rosso type, which are exposed from Turkey in the east to the Pyrenees in the west and also recovered by drilling in the North Atlantic, were the best-studied. In Russian literature, they are

described by Patrunov (1988). As a rule, these rocks are red, yellow, and brown limestones with distinct lumpy, nodular, less commonly thin-layered, and, even more rare, massive structures, with micrograined texture, and a peculiar association of fossil remains including ammonites, belemnites, planktonic and benthic foraminifers, radiolarians, coccolithophorids, calpionellids. In addition to planktonic forms, benthic, always specific groups: *Posidonia*, *Daonella*, rare Gastropoda, Spongia, and Ostracoda are also common.

According to different estimates, the sedimentation rate varies from 0.4 to 5 mm/ka, which is comparable with the accumulation rates of Cenozoic oceanic sediments of similar composition. The second half of the Cretaceous was marked by the blooming and mass development of coccolithophorids and, accordingly, by intense accumulation of nannofossil ooze. This resulted in the sharp increase in carbonate accumulation and in deposition of the specific chalk formation; the latter played a substantial and important role among all carbonate formations. It not only determined the carbonate accumulation in oceanic basins, but spread also in shelf seas covering ancient and young platforms, where pelagic deposits occupy spacious areas from the England coast to Denmark, northern Germany, East European Platform, the Caucasus, the north Caspian region, and Ustyurt.

The Cenozoic was characterized by the further shift of carbonate accumulation to oceans. Shelf seas with carbonate accumulation became rare and, more importantly, limited in size, particularly in their width. For instance, such Cenozoic basins in the Gulf of Mexico and Florida Peninsula region stretch over a distance of approximately 800 km and are not more than 200 km wide. A similar basin in the Yukatan Peninsula area was 600–650 km long and about 200 km wide.

A number of carbonate platforms also decreased. Amid the best-studied structures exist the Great Bahamas Bank, where evolution of initiated platform in the Mesozoic continued. The Cenozoic structures are represented by the Maldives Archipelago platform, marked by formation of "classic" flat-top platform during the Early Eocene–Early Oligocene, whose morphology changed in the Late Oligocene–Pleistocene (Purdy and Bertram, 1993).

Due to the decrease in a number and dimensions of shelves and isolated platforms, the significance of reefs increased. Oceanic reefs evolved during the entire Cenozoic, but their most intense development commenced in the Eocene. Pelagic carbonate accumulation in oceanic basins sharply increased both relatively and absolutely. Carbonate accumulation was almost completely pelagic at the expense of planktonic organisms: coccolithophorids, pteropods, and foraminifers.

The quantitative role of different settings is debatable. According to Lisitsin (1978), about 80% of carbonate substance is accumulated in the pelagic realm of the World Ocean, whereas the remaining 20% accumu-

lated in marginal seas and on shelves, including reefs. Different estimates were cited by Smith (1978). According to his data, reefs occupy only 0.32% of the modern carbonate accumulation area, but they accumulate almost half of the total Ca entering the ocean. Milliman (1974) believed that calcareous foraminiferal–nannofossil and pteropod–nannofossil sediments of the pelagic realm enclose 78.2% of the total carbonate material contained in bottom sediments of the modern World Ocean. Siliceous and clayey pelagic sediments, sediments of the continental slope, and reefs contain 11.2, 5.8, and 1.0% of carbonates, respectively. When the carbonate accumulation intensity is calculated for different facial zones considering their distribution areas, it appears to be minimal precisely on shelves; on reefs, it is 5.4 times higher and in the pelagic realm, it is 4.3 times higher. With regard to the approximate character of such calculations, the absolutely preponderant part of modern carbonate accumulation (and largely, of the Cenozoic as a whole) is provided by planktonic microorganisms in pelagic domains, the significant part is related to reefs, and only the insignificant part is related to other zones.

Thus, the widely-shared opinion that main carbonate accumulation is related to stable ancient platforms appears to be insufficiently correct. This statement is completely true concerning the Paleozoic epicontinental seas with spacious shelves, which accumulated carbonate sediments, but it needs substantial corrections for the Mesozoic and, particularly, the Cenozoic, when carbonate accumulation distinctly shifted into oceanic pelagic domains and when bethogene carbonate precipitation gave way to the plankton-related one.

The fact of the carbonate accumulation shift from continental blocks to oceans poses a question about its causes. Four main factors could probably be responsible for this phenomenon: (1) the absence of oceans in the Paleozoic; (2) the high CCD level stand in Paleozoic oceans, which determined the absence of carbonate material in deep-sea bottom sediments; (3) the absence of oceanic shelves in the zone favorable for carbonate precipitation during the Mesozoic and Cenozoic; and (4) the principal change in carbonate-producing organisms.

Surprisingly, the solution to the problem of the existence or absence of Paleozoic oceans largely depends on the definition of the term "ocean." Different views of specialists in tectonics and lithology were discussed by Timofeev and Kholodov (1984), who rejected an idea of the existence of Paleozoic oceans. Some statements made by these authors, in particular, the ones about the shallower depth of Paleozoic basins and absence of complete analogues of modern abyssal sediments in the Paleozoic, the acceleration of the subsidence, and the increase in relief differentiation in the geological history provoke no principal rejections. However, it should be noted that Paleozoic deep-water pelagic sediments are recorded in sufficiently wide

areas, but they are characterized by clayey, clayey-siliceous, and calcareous-siliceous-clayey, not pure carbonate composition. In other words, the cause of the phenomenon mentioned above is not the absence of spacious deep-water basins.

This phenomenon cannot be explained by the high CCD level stand. The point is that many deep-sea oceanic formations are variably calcareous, i.e., the carbonate material entered into oceans and was preserved. Paleozoic deep-sea purely carbonate sediments are rare as compared with the Mesozoic and Cenozoic; it is important that they are characterized by a distinct genetic pattern, and they did not provide pelagic carbonate sequences comparable in the thickness with those in later epochs.

The paleogeographic factor of global tectonics, i.e., position of lithospheric plates seems to be more important. Virtually no shelves, where benthogene carbonate sediments could accumulate, were preserved in the Mesozoic and Cenozoic after closure of the sublatitudinal Tethys. Spacious shelves of the young Arctic Ocean were unfavorable for carbonate accumulation due to climatic conditions. In the newly formed and expanding Atlantic Ocean, shelves were too narrow. Besides, an additional factor that strongly influenced benthogene carbonate accumulation appeared: at least since the Miocene, upwelling commenced to be active along the African coast of the Atlantic (Emel'yanov *et al.*, 1989). The influx of deep-cold waters undersaturated with carbonates suppressed the benthic life and, accordingly, carbonate accumulation. Dilution of carbonates by the terrigenous and siliceous (diatom) material also negatively influenced carbonate accumulation, which was responsible for the formation of the litho-geochemical carbon-phosphate-opal association (Emel'yanov, 1982). Benthogene carbonate accumulation in this ocean is developed only on its western shelves where upwelling is lacking. The similar situation is characteristic of the Pacific and, to a lesser extent, Indian oceans.

It is important to note that carbonate-producing organisms also changed in parallel with changes in paleogeographic settings. The causes of this biological phenomenon are beyond the scope of the paper. However, it is reasonable to pose the question: was this change, at least partly, related to global geological events? Due to the relative reduction of shelf areas in the warm climatic zone, where carbonate-producing benthic organisms were abundant, carbonates from sea water were extracted by planktonic organisms, first by algae, which became a principal carbonate-producing group. Inasmuch as algae are more tolerant to temperature conditions, they occupied also temperate-latitude basins, and as a result, chalk formation covered spacious platform areas, including those distant from the tropical zone. The aforesaid is only one of possible assumptions and represents a topic for discussion rather than an ultimate conclusion.

The shift of main areas of calcium carbonate accumulation to oceans poses a question about the correction of available concepts on evolution of the carbonate accumulation scale. If we suppose that carbonate sediments in Paleozoic oceans were limited and subsequently reduced owing to subduction and collision, then the total initial volume of carbonate rocks throughout the world, including modern continents, will increase insignificantly. In the Late Mesozoic, the volume of carbonate rocks in the continental segment should be added by the significant volume of oceanic carbonate sediments. In other words, it should be admitted that a total volume of carbonate rocks and, particularly, an intensity of carbonate accumulation significantly grew through time. This conclusion about the global distribution of carbonate rocks significantly differs from the recent concept of the wider development of carbonate rocks in the Paleozoic, as compared with the Mesozoic-Cenozoic. The latter concept is mainly based on the study of continents located in the northern hemisphere, where, according to Ronov's data, carbonate rocks are distributed wider than on Gondwanan continents (17.3 versus 10.2% in the Neogene and 17.83 versus 11.69% in the Phanerozoic, respectively). This difference is even more noticeable for platforms: carbonate rocks on the Laurasian platforms compose 44.0% of the sedimentary cover, whereas those of Gondwana make up only 10.8%.

The possible factors responsible for the intensification of carbonate accumulation under the change in the association of carbonate-producing organisms can be due to the rate of reproductivity and generation replacement, as well as metabolism of microorganisms including extraction of the mineral substance from water for constructing skeletons, which are many times higher as compared with those typical of multicellular organisms that form the basis of the benthic carbonate-producing fauna.

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Organic Matter in Oligocene Maikop Sequence of the North Caucasus

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Abstract—The results of the thorough study of organic matter (OM) in the Oligocene–Miocene Maikop sequence of the North Caucasus are considered. It is shown that its distribution within the Maikop sequence is characterized by irregular patterns. Despite that these rocks show the elevated TOC content, their hydrocarbon-generating potential is, as a rule, low. The low quality of OM is partly related to its intense anaerobic decomposition in anoxic environments with terrigenous sedimentation. The elevation of OM concentrations and hydrocarbon-generating potential could be connected with the reinforced phytoplankton influx into sediments. Sediments deposited in the second half of the Early Oligocene were synchronously enriched in OM. This enrichment chronologically corresponded to the restoration of connection with the World Ocean of the formerly partly isolated and freshened basin. Most probably, this event resulted from the sharp increase in biological productivity.

The Maikop Group is a thick mostly clayey sequence deposited during the Oligocene–Early Miocene in the epicontinental basin of the Eastern Paratethys. It represents a main oil-generating formation of the Crimean–Caucasian region and is intensely studied over many years. Some aspects of organic geochemistry of the Maikop Group were discussed in (Arkhangel'skii, 1927; Gimpelevich, 1959; Zhabrev, 1959; Pol'ster *et al.*, 1960; Sidorenko, 1964; Larskaya, 1965, 1966; Fadeeva, 1973; Vassoevich *et al.*, 1969; Geodekyan *et al.*, 1985; Khramova, 1987; Sokolov *et al.*, 1990; Bazhenova *et al.*, 1997). The stratigraphic subdivision of the Maikop Group represented a serious problem for a long time. This is explained by the fact that “typical” uniform Maikop clays with fish remains contain scarce carbonate plankton fossils. The first stratigraphic schemes of the Maikop Group, mainly based on benthic foraminifers and mollusks, often had regional and facies limitations. Such a situation aggravated investigations in other fields of geology and reliable correlation of empirical data. At present, this problem is generally solved. The abundance of material on benthic faunal groups and achievements in the study of organic-walled phytoplankton, carbonate nannoplankton, spores, and pollen allowed detailed local stratigraphic scales of the Maikop Group to be elaborated and a regional stratigraphic scale of the Eastern Paratethys to be proposed (Popov *et al.*, 1993a; 1993b). Later, Zaporozhets (1998a) suggested the regional zonal scale (based on dinoflagellates) that was correlated with the dinoflagellate scale of West and Central Europe. Thus, a modern state of the Maikop Group stratigraphy makes it possible to thoroughly study

organic matter from Maikop sequences in order to establish both lateral and vertical distribution of formations with the highest oil-generating potential and to interpret environments favoring their accumulation.

This work presents results of the study of OM in the Maikop rocks from the following structural–facial zones (Stolyarov, 1991) of the Ciscaucasia region (Fig. 1): (1) the inner shelf of the basin consisting of sediments penetrated by Borehole 45A in Northern Ergeni; (2) the Kuma transitional zone between the outer shelf and the deep-water part of the basin (in the south of the area); and (3) the presumably deeper-water part of the basin located at the maximum distance from the main provenance and best studied in the section along the Belaya River. Inner parts of the basin most likely differed from each other by sedimentation rates and proportions of the material from the northern (platform) and southern (Caucasian) provenances.

METHODS

A complex of geochemical, petrographical, and palynological investigations was carried out. Geochemical studies included the following analyses: Rock-Eval pyrolysis with a Osa device, determination of the bitumen content (extraction by chlorophorm in the Sockslet unit), gas–liquid chromatography, and element analysis of kerogen. The Rock-Eval pyrolysis method proposed by Espitalie *et al.* (1985–1986) includes heating of about 100 mg of disintegrated rock to 600°C in the inert atmosphere and under the programmed temperature regime (25°C/min). The method makes it possible to register the following parameters:

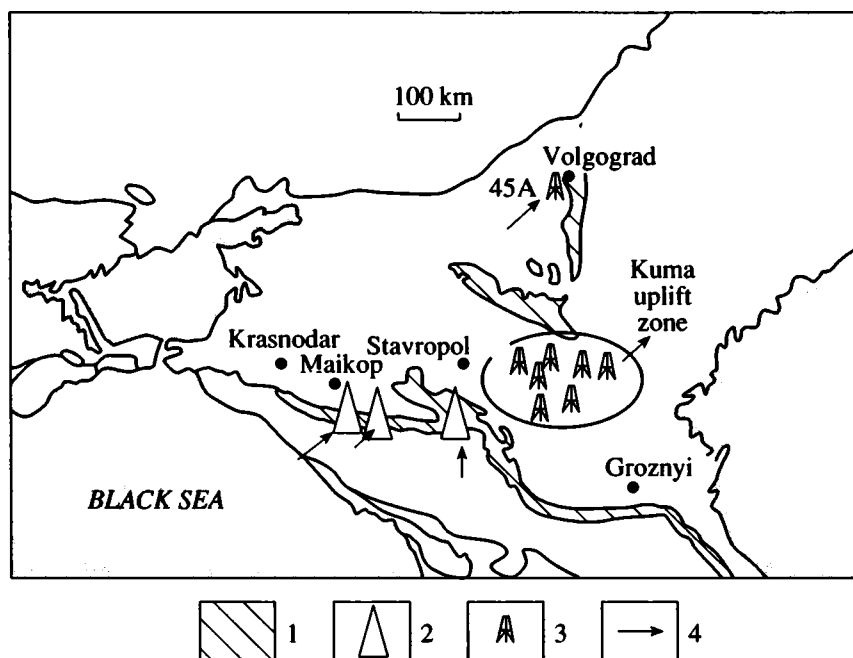


Fig. 1. Schematic distribution map of Maikop sediments in the Ciscaucasia region and location of studied section.
(1) Argillites; (2) outcrops; (3) wells; (4) location of the studied sections.

(S_1) quantity of free hydrocarbons (oil + gas) separated at temperature below 300°C (mg/g rock) and (S_2) quantity of hydrocarbon (HC) compounds formed in the temperature interval of 300 to 600°C as a result of kerogen cracking (mg/g rock); the sum of S_1 and S_2 peaks representing the HC-generating potential of studied rocks, which is usually expressed as kg OM/t rocks; ($T_{\max}$) the temperature at the top of the S_2 peak indicating thermal maturity of OM (°C); (TOC) the total organic carbon, which is equal to the sum of pyrolysis-subjected and remnant organic carbon (%); and (HI) hydrogen index corresponding to S_2 /TOC ratio (mg OM/g TOC).

The hydrogen index directly correlates with the content of alyphatic structures in kerogen. Thus, it indicates kerogen quality and reflects HC-generating (henceforth, HC) potential of organic matter. It is high in marine, purely algal OM and inversely correlates with terrestrial component in the organic matter.

The petrographic analysis included the study of thin sections of rocks and different components of insoluble OM extracted in the course of the successive treatment of rocks by hydrochloric and fluoric acids and maceration in the heavy liquid. The study of organic matter was performed in two aspects: (1) organic macerate

Table

Series	Subseries	Zones based on the dinoflagellate assemblage		Local subdivisions		
				Northern Ergeni (Borehole 45A)	Kuma Uplift zone	Belaya River
OLIGOCENE	Upper	Ch.p.	D.s.	Kalmyk Formation, 85m	upper part of the Middle Miocene (undivided Middle Maikop), >100 m	Septarian Formation, 100 m
			R.d.		Batalpashinsk Formation, >60 m	Batalpashinsk Formation, 60 m
	Lower	W.g.		Ikiburul Bed, 45 m	Morozkina Balka Formation, 30 m	Morozkina Balka Formation, >100 m
				Ostracoda Bed, 0.5–20 m		
		W.s. P.a.	B-H	Tsimlyansk Formation, 125 m	Psekha Formation, 15 m	Psekha Formation, 25 m

Note: P.a.—*Phthanoperidinium amoenum*; W.S.—*Wetzeliiella symmetrica*; B-H—*Batiacasphaera-Hystrichokolpoma*; W.g.—*Wetzeliiella gochii*; R.d.—*Rhombodinium draco*; D.s.—*Deflandrea spinulosa*; Ch.p.—*Chiropteridium partispinatum*.

was described and subjected to the semiquantitative analysis with the determination of proportions of its different components: amorphous organic particles, fragments of plant remains, coaly particles, microscopic resin particles, spores and pollen, microphytoplankton, chitinoïd microforaminifers, and other organic remains; and (2) the detailed analysis of taxonomy of organic-walled phytoplankton, spores, pollen, and determination of their age.

RESULTS AND DISCUSSION

Borehole 45A

Borehole 45A (Northern Ergeni), drilled in the marginal inner shelf of the basin, penetrated three Oligocene formations of the Maikop Group. Miocene sediments are completely eroded (Fig. 2).

The Tsimlyansk Formation. Lower Tsimlyansk Subformation. The lower part of the subformation is composed of thin-laminated dark-gray clay with carbonate interbeds and clayey nodules. The middle part is represented by dark-gray thin-laminated clay with siltstone interbeds containing fish scales. The upper part of the subformation corresponds to dark-gray, almost black clay with sprinklings of the silty material at bedding surfaces. All of these rocks bear dinoflagellate assemblages of the *Phthanoperidinium amoenum* Zone (Zaporozhets, 1998b) or D13 Zone of the West European scale by Costa and Manuma (*The Northwest...*, 1988).

The Upper Tsimlyansk Subformation. The unit is composed of dark-gray clay with interbeds of more silty varieties. The upper part is marked by pyrite nodules. The dinoflagellate assemblage indicates undivided *Wetzeliiella symmetrica* and *Wetzeliiella gochtii* zones corresponding to the D14 Zone by Costa and Manuma (*The Northwest...*, 1988).

The Solenov Horizon. Ostracoda Bed. The section is represented by massive silty clay with the marl bed at the base. Organic-walled phytoplankton allows the *Batacasphaera* and *Hystrichokolpoma* beds to be distinguished within the undivided *Wetzeliiella symmetrica* and *Wetzeliiella gochtii* zones.

The Ikiburul Bed. The unit corresponds to intercalating dark-gray silty clay and siltstone with the dinoflagellate assemblage of the undivided *Wetzeliiella symmetrica* and *Wetzeliiella gochtii* zones.

The Kalmyk Formation. The formation is composed of clay and siltstone with furoids. The base of the formation is marked by siltstone with light-colored sand interbeds. Most of the formation is characterized by the dinoflagellate assemblage of the *Rhombodinium draco* Subzone of the *Chiropteridium partispinatum* Zone, whereas the upper layer belong to the *Deflandrea spinulosa* Subzone of the same zone (Zaporozhets, 1998b) or to the D15 Zone of the scale by Costa and Manuma. The Kalmyk Formation is overlain by Pliocene Ergeni sands.

The TOC content in studied samples ranges between 0.3 to 3.1%. The Lower Tsimlyansk sediments are characterized by its persistently elevated concentrations (> 1%). However, low hydrogen index (HI) values indicate its low potential. The HC potential, i.e., the amount of hydrocarbons generated in these rocks during the entire catagenetic evolution, is very low (less than 1 kg HC/t rocks). In the upper part of the Tsimlyansk Formation, the OM content falls, and in overlying strata, it is only tenth fractions of percent. The only exception is a sample from the lower part of the Ostracoda Bed. In the latter, the TOC content amounts to 9.2%. This stratigraphic level is characterized by the high HC potential (10 kg HC/t rocks). Simultaneously, low values of HI indicate the preponderance of terrestrial OM in the considered sample. This is confirmed by the results of petrographic investigations: more than 95% organic macerate are represented by sufficiently large plant fragments.

The Kuma uplift zone

With regard to the structure, this zone located in the platform part of the Eastern Ciscaucasia represents an uplifted block in the eastern part of the Stavropol arch (Yudin, 1977). To the east, the zone can be traced to the Caspian Sea; in the north, it is bounded by the Eastern Manych trough; and in the south, by the Kizlyar scarp that dips into the Terek-Caspian foredeep. The Maikop Group is usually situated in this region in the depth interval of 2000–3000 m and at 4000 m in the southern part of the considered zone. Its thickness amounts to 1000 m including 40–50 m of the Lower Oligocene rocks. Studied samples were collected from the following boreholes: Iskrinskaya 5; Aleksandrovskaya 4, 5; Zhuravskaya 78, 82; Achikulak 64, 65; Novomolodezhnaya 3; Emel'yanovskaya 1; Elgashskaya 1; Sovetskaya 19, 21; Kurskaya 10; and Mozdok 6. Their characteristics are given separately for every constituent formation. However, it should be noted that the core material was, unfortunately, inaccessible for the direct study; therefore, we could not perform lithological and palynological analyses.

The Pshekha Formation is represented by dark-gray laminated clay with planktonic foraminifers. The TOC content ranges between 2 and 6% (Fig. 3). The HC potential of these rocks varies from medium to high (5.5–21 kg HC/t rocks). Moderate HI values (100–300 mg HC/g TOC) most likely indicate the mixed (marine and terrestrial) origin of organic matter. The organic macerate is largely represented by accumulations of a brownish yellow amorphous substance (> 95%) and rare microphytoplankton (dinoflagellates, prasinophyte algae). Single pollen grains are present as well.

The Ostracoda Bed. This unit is composed of marl (assumed from log analysis, samples are missing) and overlying beige-gray dark clay. The dinoflagellate assemblage from marl of the Solenov Horizon of the adjacent areas is very similar to that from the Ostracoda

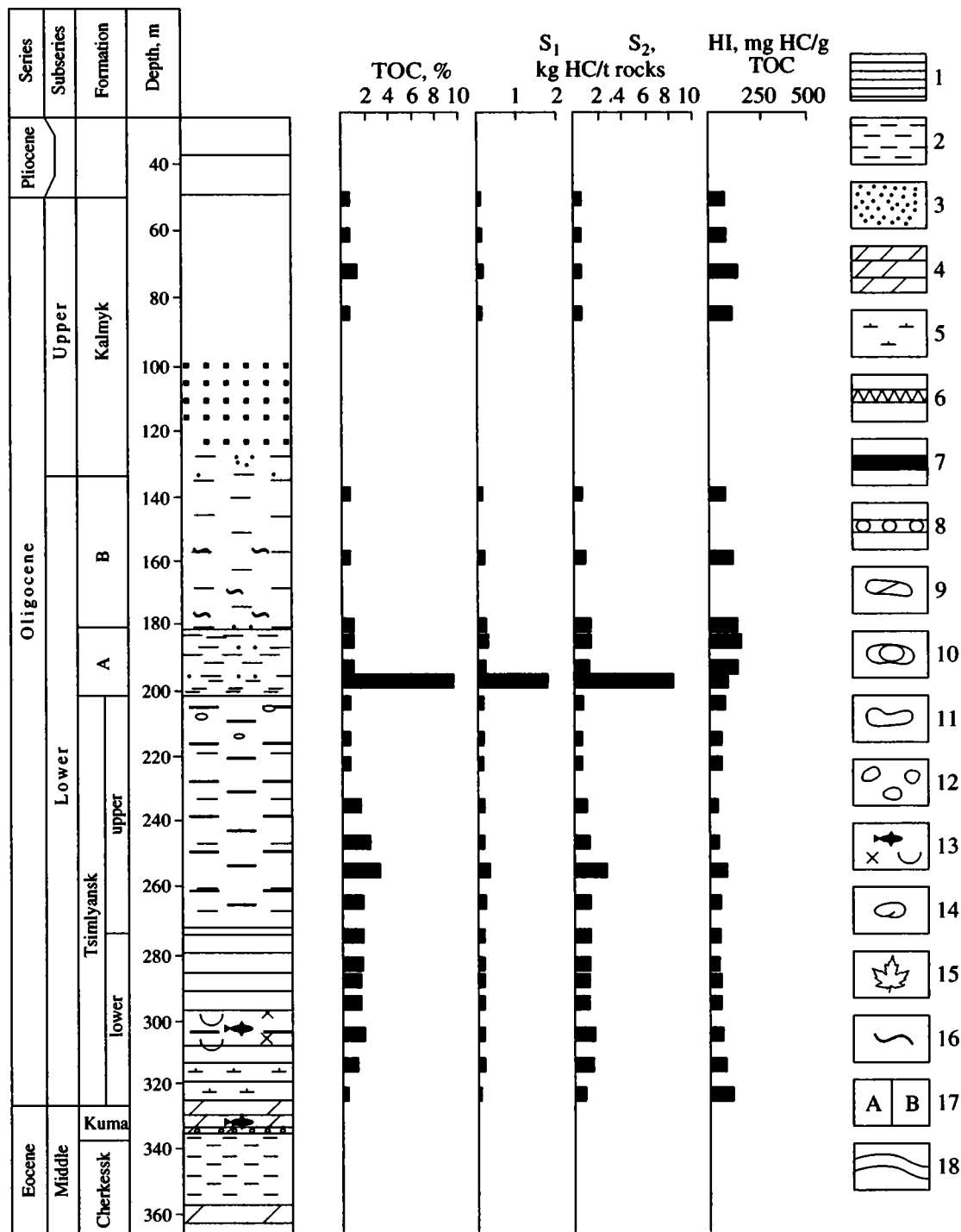


Fig. 2. Lithochemical section of Maikop sediments, Well 45A, Northern Ergeni.

(1) Clay; (2) siltstone; (3) sand; (4) marl; (5) carbonate rocks; (6) ash interbeds; (7) coal seams; (8) pebble and gravel; (9) marly concretions; (10) Septarian concretions; (11) siderite concretions; (12) pyrite nodules; (13) fish remains; (14) pteropods (*Planorbella*); (15) plant remains; (16) fucoids; (17) subdivisions of the Solenov Formation: (A) Ostracoda Bed, (B) Ikiburul Bed, (18) hiatuses.

Bed of the North Caucasus. Preponderant are *Batiacaphaera* species (> 95%) including *B. sphaerica*, *B. baculata*, and *B. micropapillata*. Single specimens of the assemblage belong to different, including thin-walled,

morphotypes of the *Hystriocholpoma* genus and also *Impagidinium*, *Adnatosphaeridium*, *Lejeunecysta*, *Selenopemphix nephroides*, *Cribroperidinium*, and *Horologinella*. This assemblage corresponds to the

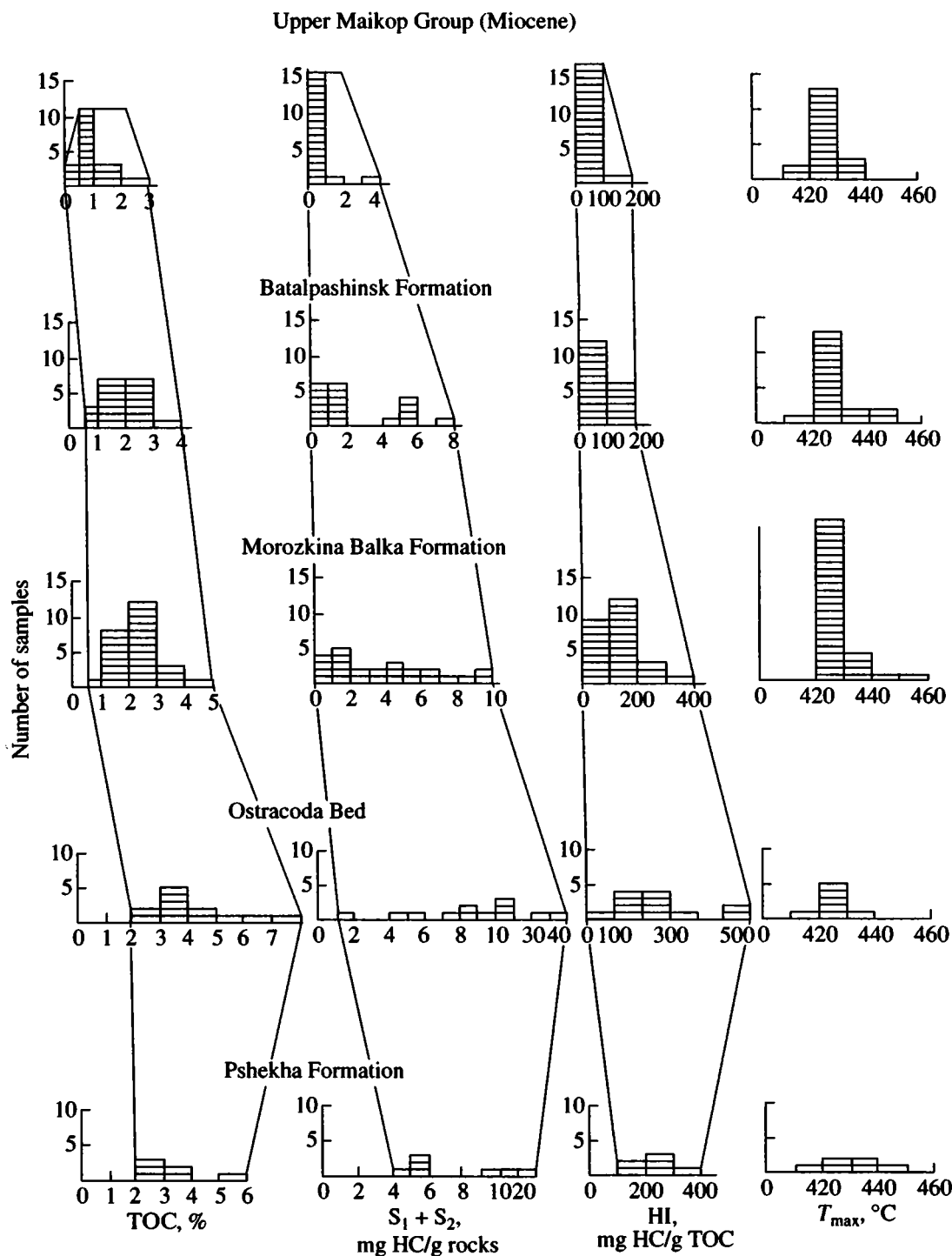


Fig. 3. Distribution of genetic parameters: organic carbon (TOC), HC potential ($S_1 + S_2$), and hydrogen index (HI) in the Maikop Group section of the Kuma uplift zone.

Wetzeliiella gochti Zone, although the zonal species itself was not recorded in the Ostracoda Bed of the studied section.

Marls are characterized by the highest concentration of organic carbon (up to 7.8%). The HC potential is high (4–8 kg HC/t rocks) in most samples and very high

(to 40 kg HC/t rocks) in some of them. The hydrogen index, which indicates the OM quality, reaches 600 mg HC/g TOC and testifies that such a high HC potential is related to the preponderant phytoplankton-related OM with the well-preserved lipid component. The organic macerate is dominated by yellow amor-

phous particles (85%). Nonetheless, it contains a sufficiently high content of microphytoplankton (dinoflagellates) and also spores and pollen.

The **Morozkina Balka Formation** is composed of dark-gray, sometimes silty clay with obscure lamination. The TOC content differs almost by an order ranging between 0.6 and 5.5%. Usually, it varies from 2 to 3% (average 2.6%). The HC potential also varies within the wide range: nine samples yield low values (< 2 kg HC/t rocks); nine samples are characterized by medium values (2–6 kg HC/t rocks); and six samples, by high values (6–20 kg HC/t rocks). The hydrogen index, however, is characterized by low values. They exceed 300 mg HC/g TOC only in the single sample (Fig. 3). Thus, the obtained data reveal that the analyzed samples enclose OM of the mixed type. Organic macerates from these rocks show the presence of abundant yellowish brown substance. Microphytoplankton, spores, and pollen are subordinate.

The **Batalpashinsk Formation**. Lithologically, these rocks are similar to clayey varieties of the Morozkina Balka Formation being more silty. The TOC contents are relatively high (average 1.8%). The HI values decrease as compared with the previous unit and are commonly below 200 mg HC/g TOC, thus, indicating that samples enclose strongly degraded organic matter. This determines also the low HC potential of rocks (0.5–4 kg HC/t rocks). The exception are samples from Borehole Aleksandrovskaya 5, which yielded the medium HC potential values (3–7.5 kg HC/t rocks). Similarly to samples from the previous unit, the organic macerate is dominated by amorphous organic matter. Nonetheless, it contains microphytoplankton and sufficiently high amounts of spores, pollen, plant fragments (sometimes, well-preserved), and coaly particles.

The **upper part of the Maikop Group (undivided)**. This interval of the Maikop Group is composed of gray silty clay and siltstone. The TOC contents are significantly lower as compared with the underlying units (average 0.9%). The HC potential is low (< 1 kg HC/t rocks). All the determined HI values are also extremely low, which makes it impossible to interpret the possible source of organic matter. In the organic macerate, the leading role belongs to cuticle remains and other fragments of higher plants as well as to spores and pollen (mainly *Pinus*).

In diagram HI- $T_{\max}$ (Fig. 4a), most of the studied samples from the Pshekha Formation, Ostracoda Bed, and Morozkina Balka Formation fall in the area that corresponds to either mixed, type II (marine) and type III (terrestrial) organic matter or degraded, type II organic matter. Nonetheless, the scatter of data points in the diagram HI-TOC most likely supports an assumption that organic matter includes the, more or less, significant admixture of terrestrial component. Several samples from the Lower Oligocene sequence distinctly yield the type II organic matter. The Batalpashinsk and younger samples from the Maikop Group correspond to

the area of highly degraded OM (type IV kerogen, according to Tissot, 1984).

The $T_{\max}^{\circ}$ values indicating the thermal maturity of organic matter vary in rocks of all above-considered units from 410 to 450°C depending on the depth of the rock occurrence. However, most samples show the $T_{\max}^{\circ}$ values ranging in a significantly narrower interval (420–430°C) indicating a low thermal maturity of organic matter.

The Belaya River section

Rocks of the Maikop Group are exposed in the Belaya River basin near the Abadzekhskaya Settlement located 23–24 km south of Maikop (Fig. 1). At present, this section is the most complete one characterizing the Maikop Group of the Western Ciscaucasia. The section has been studied during many years (Korotkov, 1935; Grossgeim and Gladkova, 1953; Grossgeim, 1960). Recently, owing to achievements of the plankton biostratigraphy, the age of some formations was determined more reliably and their range and boundaries were specified (Krhovsky *et al.*, 1995; Zaporozhets, 1998a). The Belaya River section comprises the following units (from the base upward):

The **Pshekha Formation** is represented by dark-gray and black carbonate laminated clays with pteropod remains in the lower part, rhythmic alternation of gray carbonate and darker slightly carbonate or carbonate-free clays in the middle part, and by dark-gray carbonate-free clays in its upper portion (Fig. 5). The lower part of the unit yields the nannofossil assemblage of the NP21 Zone and dinoflagellate assemblage of the *Phthanoperidinium amoenum* (D13) Zone. The middle part contains dinoflagellates of the *Wetzeliaella symmetrica* (D14a) Zone. The upper part of the formation is characterized by dinoflagellates and nannoplankton correlating it with the *Wetzeliaella gochti* (D14b) Zone and NP22 Zone, respectively.

Sediments show slightly elevated and sufficiently uniform TOC contents ranging from 1.7 to 2.4%. However, the general HC potential of these rocks is not high (0.8–4.5 kg HC/t rocks). The HI values are also low (< 206 mg HC/g TOC). The pyrite-related Fe content varies from 0.1 to 1.3%. The organic macerate contains preponderant accumulations of amorphous grayish-brownish OM (60–90%), common microphytoplankton, spores, pollen, and subordinate fragments of plant remains usually substantially degraded, as well as shells of microforaminifers.

The **Polbinka Formation** (Ostracoda Bed) is composed here of white marl (the Polbinka Bed) with ostracod remains. This bed represents a regional reference layer. Nannoplankton from these rocks correlates with the NP23 Zone counterport. The peculiar dinoflagellate assemblage indicating abnormal, most probably highly freshened, hydrochemical environments includes *Bati-*

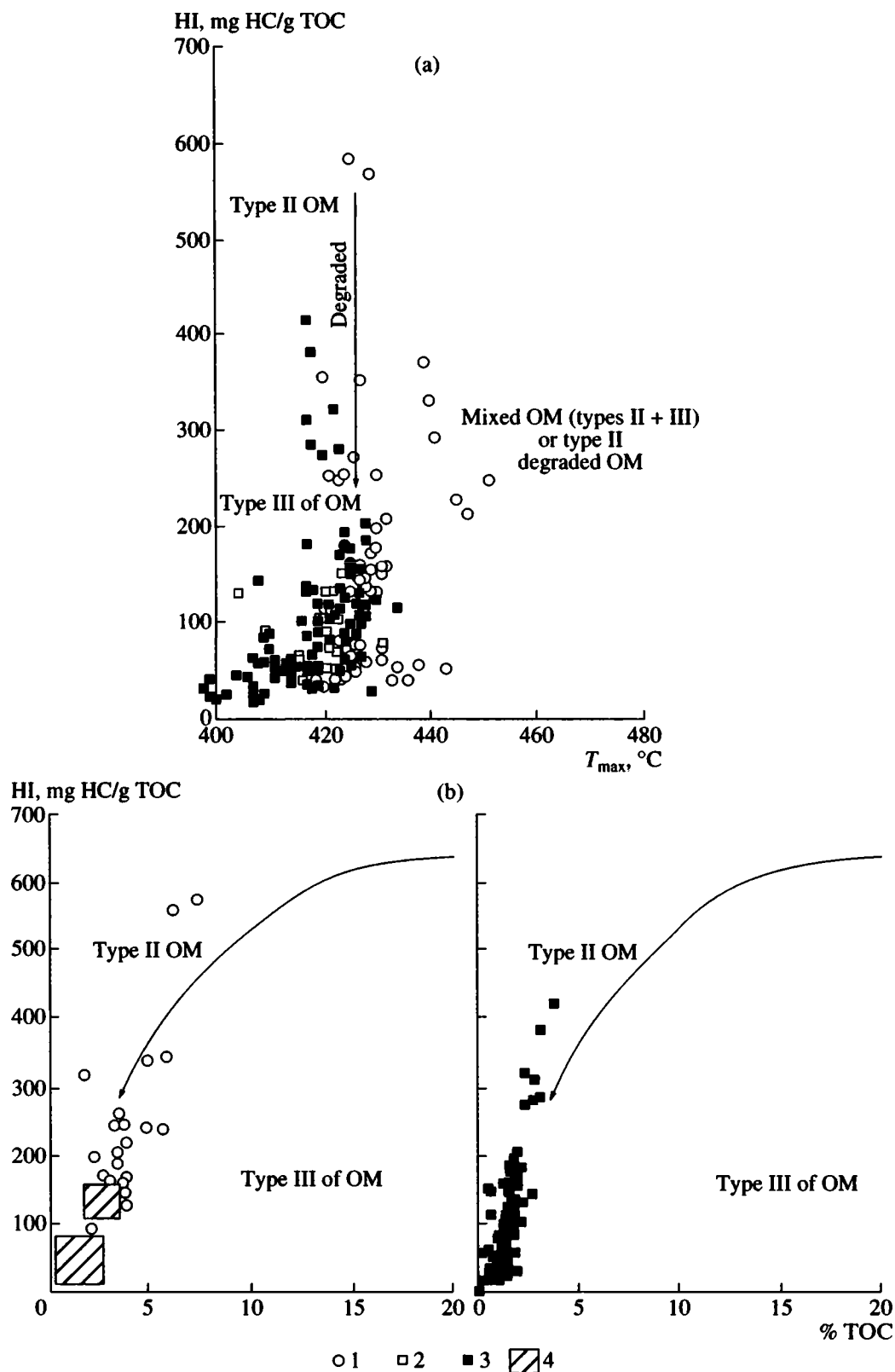


Fig. 4. Relationships of hydrogen index (HI) in Maikop rocks with: (a) T_{max} , °C and (b) organic carbon content, TOC. Data obtained from wells: (1) Kuma uplift zone, (2) Northern Ergeni (45A); (3) outcrops, Western Ciscaucasia; (4) domains with 10 or more measurements of HI and OM content.

acasphaera spp. and *Hystrichokolpoma* spp. (up to 80% of the assemblage, including thin-walled morphotypes of small dimensions). This assemblage is distinguished as *Batiacasphaera* and *Hystrichokolpoma* beds of the *Wetzeliiella gochtii* Zone. The carbonate content in these sediments is 70.5% (Fig. 5). The TOC content is sufficiently low (0.5%). The organic macerate contains abundant microphytoplankton, pollen, spores, and plant fragments of the variable preservation degree.

The **Morozkina Balka Formation** is subdivided into two subformations. The lower subformation consists of dark brownish gray carbonate-free clay covered by jarosite at the surface. Oval carbonate concretions (30 × 10 cm) occur in the upper portion of the unit. No nannofossils are recorded (Zaporozhets, 1998a). Similarly to underlying sediments, dinoflagellates correspond to the *Wetzeliiella gochtii* Zone.

The TOC content is persistently characterized by elevated values (1.4–2.9%). However, the HC potential of these rocks varies from 0.7 to 8.9 kg HC/t rocks. The HI values range within the interval of 111–287 mg HC/g TOC. Nonetheless, rocks from the basal part of the formation are characterized by the maximum TOC contents, (3.8%) among all studied samples (Fig. 5). The HI values amount at this level to 420 mg HC/g TOC, testifying to good preservation of marine (phytoplankton and bacterial) organic matter. The considered sediments are characterized by the high HC potential (16 kg HC/t rocks). The organic macerate is mainly (95%) formed by accumulations of amorphous OM of orange–brown coloration.

The upper subformation is represented by slightly carbonate brownish gray clay with jarosite. The lower part of the subformation contains nannoplankton assemblage of the NP23 Zone and dinoflagellates of the *Wetzeliiella gochtii* Zone, whereas its upper portion is characterized by nannoplankton of the NP24 Zone and dinoflagellate assemblage correlative to the *Rhombodinium draco* Subzone of the *Chiropteridium partispinatum* Zone.

Concentrations of organic carbon recorded in the considered samples are characterized by sufficiently uniform values (1.24–1.8%). The HC potential is medium (1.5–3.4 kg HC/t rocks). The HI values are low (108–179 mg HC/g TOC).

The **Batalpashinsk Formation** is formed by dark–brown jarosite-bearing clay with rare siderite and marly concretions. Nannoplankton is not recorded (Krhovsky *et al.*, 1995; Zaporozhets, 1998a). Dinoflagellates are referred to the *Chiropteridium partispinatum* (D15) Zone (the *Rhombodinium draco* Subzone in the lower part and the *Deflandrea spinulosa* Subzone in the upper portion).

The TOC content ranges from 0.7 to 1.7% (Fig. 5). The HC potential is insignificant with maximum values of 2.5 kg HC/t rocks. Values of HI are also low, thus,

preventing interpretation of the genesis of initial organic matter.

The **Septarian Formation** is composed of carbonate-free clay and siltstone. The boundary with the underlying stratigraphic unit is sufficiently tentative and corresponds to the appearance level of marly concretions with septarians that are persistent through the section. The section encloses well-sorted medium-grained sand interbeds. The upper layers of the formation enclose the nannoplankton assemblage characteristic of the transitional interval between the NP25 and NN1 zones. This part of the Septarian Zone corresponds to the *Labyrinthodinium truncatum* dinoflagellate zone, the lower part of which is also characterized by the occurrence of *Deflandrea spinulosa*. The assemblage of this zone can be correlated with the assemblage D16 of the West European scale by Costa and Manuma. However, the species, which we suggest to consider as representing the zonal one, usually appears in the European sections only in the Lower–Middle Miocene boundary interval. The contact of the Septarian Formation with the overlying Karadzhhalga Formation corresponds with the level of disappearance of concretions.

The TOC content varies from 0.7 to 1.6%. The HC potential is insignificant (0.2–2 kg HC/t rocks). The HI values are also extremely low (50–100 mg HC/g TOC). The organic macerate is dominated by amorphous, highly pyritized organic matter. Pollen and spores are also common, whereas microphytoplankton and plant fragments are subordinate. The pyrite-related Fe content is sufficiently uniform throughout the section (1.1–1.3%).

The **Karadzhhalga Formation** consists of carbonate-free laminated gray silty jarosite-bearing clay. The nannoplankton assemblage is referred to the NN1 Zone. Dinoflagellates correlate sediments with the lower part of the *Labyrinthodinium truncatum* (D16) Zone containing *Deflandrea spinulosa*, which allow them to be dated as the Aquitanian.

The TOC content ranges within the same interval as in the underlying sequences: 0.8–2% (Fig. 5). Except for a single sample showing the medium HC potential (4.5 kg HC/t rocks), all studied samples are characterized by its low values (less than 1 kg HC/t rocks). The HI values are negligible (25–87 mg HC/g TOC) and, thus, provide no information. The organic macerates of the sample from the basal part of the formation contains a significant amount of cuticle fragments (10%) against the background of dominant amorphous organic matter. Higher in the section, the preponderant role passes on plant remains, spores, and pollen. The topmost sample is again dominated by accumulations of grayish brown amorphous organic matter. Simultaneously, the pyrite-related Fe content decreases to 0.4% in this sample.

Three millimeter-thick black coaly laminae occur in the considered section: one in the Pshekhha Formation and two in the Septarian Formation. These laminae are

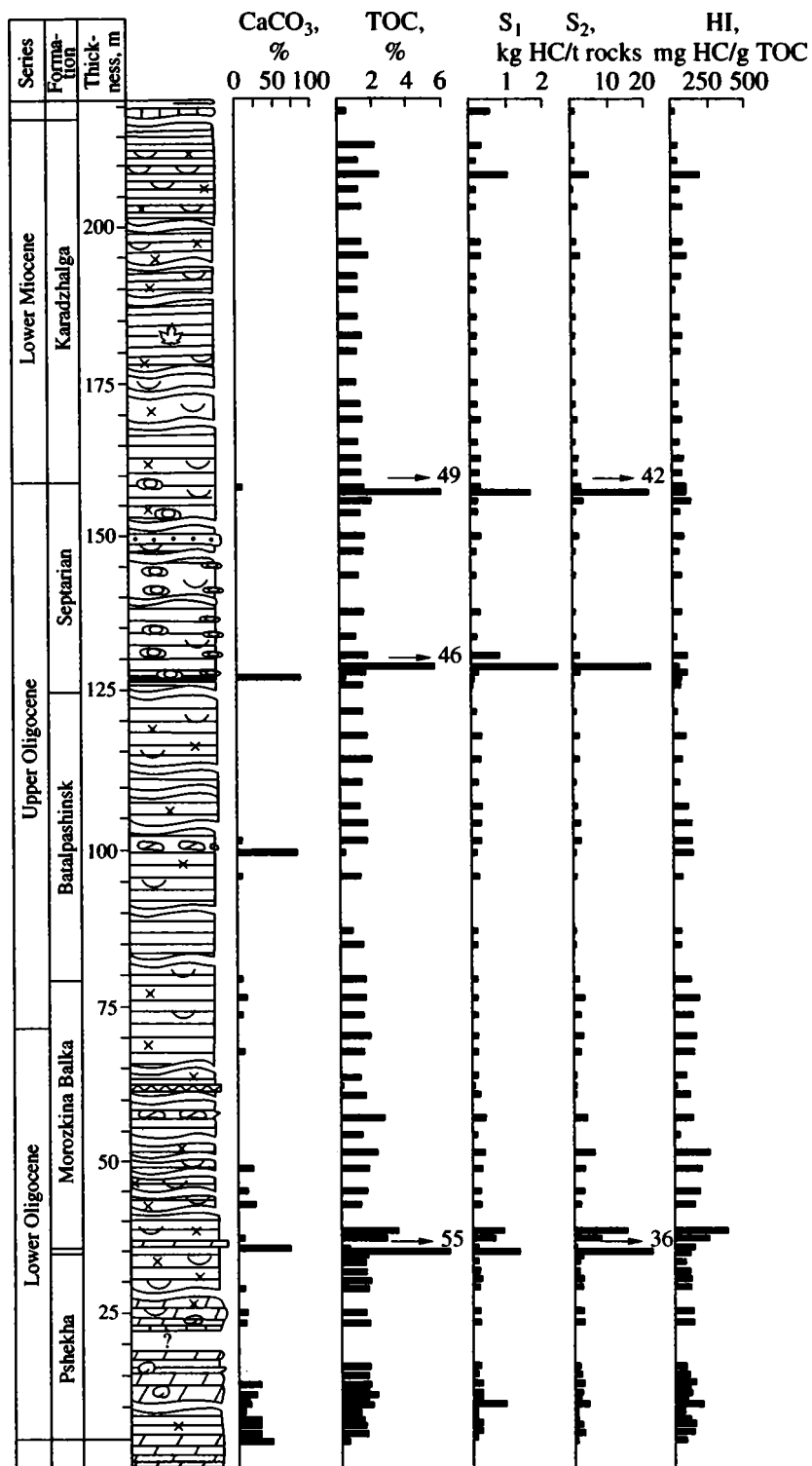


Fig. 5. Lithogeochemical section (Belaya River). For legend see Fig. 2.

characterized by the elevated TOC content, 50–57% (Fig. 5). Their HC potential is high (20–45 kg HC/t rocks). The HI values, however, are very low and typical of coals.

Organic matter of all studied samples reveals a low degree of the thermal maturity ($T_{\max} < 430^\circ\text{C}$).

In diagram HI– $T_{\max}$ (Fig. 4b), the richest samples fall into the area of the type II (marine) organic matter.

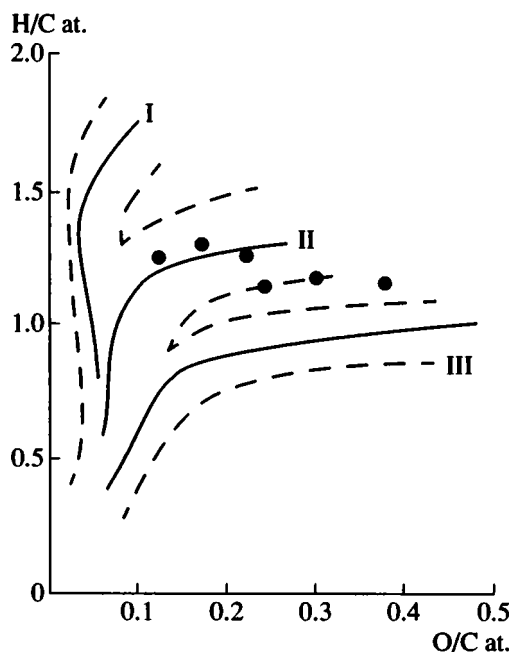


Fig. 6. Van-Krevelen diagram (H/C and O/C atomic ratios) for the Maikop Group kerogen.

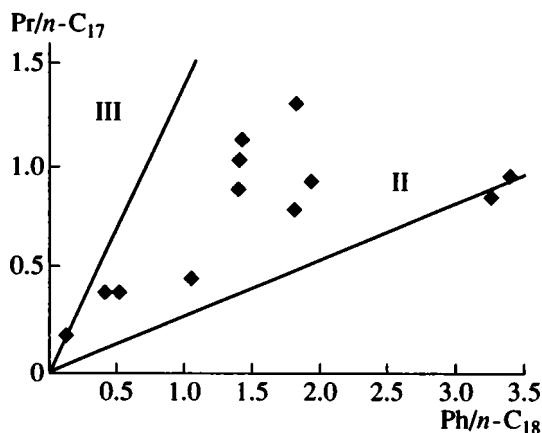


Fig. 7. Pr/n-C₁₇ vs. Ph/n-C₁₈ in hydrocarbon fraction of organic matter (by G. Connan-A. Kassow diagram).

However, most samples fall into the area, which corresponds either to mixed, types II and III (terrestrial) organic matter or to highly degraded, type II organic matter. Nevertheless, the linear correlation between the OM content and HI value favors the latter assumption.

In Van-Krevelen's diagram (Fig. 6) that allows a type of organic matter to be determined based on the atomic relation of hydrogen, oxygen, and carbon in kerogen, all studied samples fall in the area corresponding to the second type 2 organic matter. This indicates that the corresponding part of the basin was mainly under the influence of the marine autochthonous OM influx.

The chromatographic analysis of oils from the chloroform bitumen revealed the bimodal distribution of

paraffin hydrocarbon of the normal structure (*n*-alkanes) and with maxima of C₁₇₋₁₈ (indicating preponderance of phytoplankton in initial organic matter) and C₂₉ and a large-scale odd pattern in the C₂₅₋₂₉ areas indicating the presence of higher plant waxes in organic matter.¹ However, the presence of the second peak and its dominance is characteristic of immature sediments even with the insignificant admixture of terrestrial organic matter. In the diagram of Connan and Cassow (1980), which determines the OM type by the ratio of isoprene alkanes (*u*-C₁₉-pristane-Pr and phytane-*u*-C₂₀-Ph, *n*-alkanes *n*-C₁₇ and *n*-C₁₈) that are eluted in one area of coefficients Pr/*n*-C₁₇ and Ph/*n*-C₁₈, samples correspond to the area of mixed OM with preponderant marine algal material (Fig. 7).

An additional study of organic matter in separate samples from Maikop Group sections outcropping along the Fars (Western Ciscaucasia) and Kuban (Central Ciscaucasia) rivers also showed that sediments occurring above the Ostracoda Bed (Polbinka Formation in the former locality and the lower subformation of the Morozkina Balka Formation in the latter locality) are characterized by highest TOC contents (up to 3%), elevated HI values (350–400 mg HC/g TOC), and high HC potential (8–11 kg HC/t rocks). According to Yu.O. Gavrillov (GIN RAS, pers. comm.), who studied the section along the Sulak River (Eastern Ciscaucasia), sediments of the Gekhi Formation immediately overlying the Ostracoda Bed are again characterized by the elevated OM content.

The comparison of the analytical data obtained for samples from three structural-facies zones reveals slight differences in organic matter characteristics, particularly in the Early Oligocene interval. In the higher portion of the sections these differences disappear. The OM content is noticeably lower (0.3–3.1%) in the marginal inner shelf zone and slightly higher (> 1.7%) in the deep-water distal part of the basin. Its maximum values are recorded in the Kuma uplift zone (2–6%). An exception is a stratigraphic level located in all three zones immediately above the Ostracoda Bed, where the OM content increases several times. Similar patterns are characteristic of the hydrogen index. Its lowest values correspond to the marginal shelf zone with the prevalent dispersed OM of the terrestrial origin. Intermediate values are recorded within intraplatform uplifts, where organic matter is characterized by mixed, terrestrial and marine composition. Finally, in relatively deep-water facies that were formed far from the provenance, the HI value amounts to maximum values in samples with mainly marine (phytoplanktonic and bacterial) organic matter. However, in this zone, organic matter is also commonly of mixed origin. The generally low HC potential is lowest in the marginal shelf zone and 2–3 times higher in the inner areas of the

¹ The subscript numbers in C₁₇₋₁₈ and C₂₉ correspond to the carbon atomic numbers in molecule.

basin. Its anomalous values are recorded in the top sediments of the Ostracoda Bed.

DISCUSSION

Recently, due to many researches (Sorokin, 1962; Romankevich, 1970; Skopintsev, 1971; *Initial Reports...*, 1978), the main factors responsible for the OM accumulation in marine sediments are listed below:

(1) Initial bioproductivity. It directly correlates with the amount of organic matter that avoided a complete mineralization in upper eutrophic layers and entered the lower layers.

(2) The depth of sedimentation basin, i.e., the thickness of water column crossed by organic matter. The duration of the biological and physicochemical degradation of OM is also a function of the depth. The formation of organomineral aggregates as well as their transit in the form of fecal pellets favors its preservation.

(3) Sedimentation rate. It has a particular importance in oxidizing settings because the higher are sedimentation rates, the less is the period of OM oxidation at the water/sediment boundary. This correspondingly results in the decreased OM loss, all other parameters being equal, and in the increased concentrations of buried organic matter. In addition, elevated sedimentation rates prevent sediments from their bioturbation. On the other hand, very high sedimentation rates result in the decreased OM concentrations in sediments due to its dilution by the terrigenous material.

(4) The redox potential of the environment (water and sediment). In most cases, sediments that were accumulated under slightly reducing (disaerobic) or reducing (anaerobic) conditions are enriched in OM as compared with sediments formed in oxidizing environments.

(5) Granulometry of sediments.

The obtained data indicate that the Lower Oligocene rocks of the Maikop Group are characterized by the relatively elevated TOC content. This is also true for rocks of Eastern Ciscaucasia (Sokolov *et al.*, 1990). Their HC potential, however, is variable (0.8–21 kg HC/t rocks).

At the beginning of the Oligocene, the Ciscaucasia region was subjected to tectonic movements that affected paleogeographic settings and sedimentation dynamics (Zhizhchenko, 1969; Stolyarov, 1991; Popov *et al.*, 1993a; *Geologicheskie ...*, 1997). These movements resulted in a significant deepening of shelf depressions and promoted sharp morphologic differentiation of the Eastern Paratethys that occurred against the background of stable hypsometric position of main positive paleogeographic structures. The differentiation and relative isolation from the World Ocean hampered water circulation in the Early Oligocene basin. According to many researchers (Stolyarov, 1991; Popov *et al.*, 1993a; Nedumov, 1994; Stolyarov and Kochetov, 1995; Popov and Stolyarov, 1997), this, in turn, led to the for-

mation of anaerobic conditions in bottom waters of deepest zones. Popov and Stolyarov (1997) believe that significant hydrogen sulfide contamination of waters, first in the Eastern Paratethys history, that resulted in the formation of giant manganese deposits at the oxygen barrier corresponded with the second half of the Pshekhian time (basal layers of the *Wetzeliella gochti* and *Spiroplectannina carinata* Zone). The almost complete absence of bottom fauna in sediments of this age is one of the main arguments favoring this hypothesis. The study of thin sections of these rocks reveals finely laminated, ichnofossil-free interbeds. According to the scale by Wignall (1994), which estimates an oxygen-saturation degree of bottom waters based on bioturbation, this indicates that the oxygen content in bottom waters during the accumulation of the upper Pshekhia sediments by no means exceeded 0.5 ml/l. According to Wilkin *et al.* (1996), who studied forms and dimensions of pyrite in different modern basins, the presence of small framboids of pyrite (< 7 μ m) in thin sections is indicative of intense sulfate reduction in the water column. Nonetheless, finds of deep-water fishes in the upper Pshekhia strata of the Ciscaucasia region (Danil'chenko, 1960; *Geologicheskie...*, 1998) do not support the hypothesis of hydrogen sulfate contamination of the significant part of the basin and allow one to speak only about anoxic conditions in bottom waters.

The anaerobic environments of the sea basin promoted an intense oxidation of OM in the course of bacterial reduction of sulfates to hydrogen sulfide. Moreover, the intensity of the sulfate reduction in the anaerobic water column is an order of magnitude higher than in sediments (Volkov, 1959, 1961a, 1961b; Volkov and Pilipchuk, 1966; Sorokin, 1962; Jorgensen, 1982; Lein and Ivanov, 1990). Henrichs and Reeburgh (1987) and Canfield (1989, 1994) showed that, under high sedimentation rates, the efficiency of anaerobic decomposition of OM is comparable with that of aerobic oxidation (under low sedimentation rates, aerobic oxidation is more effective). The absence of the direct dependence between the intensity of sulfate reduction and TOC content was noted by many researchers (Gulyaeva, 1953; Volkov, 1961b; Volkov and Pilipchuk, 1966; Richard, 1976; Ivanov *et al.*, 1980). In opinion of the latter authors, the intensity of bacterial sulfate reduction is controlled by the quantity of organic compounds accessible for microorganisms in organic matter but not by its bulk content. According to Laanbroeck and Veldkamp (1982), anaerobic microorganisms can consume only some organic substrates. Some classes of organic compounds (for instance, formaldehyde and some polymer aromatic compounds) can be oxidized only in the presence of molecular oxygen and are inaccessible for anaerobic bacteria or their decomposition in anaerobic conditions is slower (Uspenskii, 1970; Berry *et al.*, 1987; Lovely, 1991; Lee, 1992; Canfield, 1994). Thus, in opinion of some authors (Uspenskii, 1970; Canfield, 1989; Tyson, 1995), contrary to aerobic oxidation, the intense anaerobic decomposition of OM is accompa-

nied by elevated remnant carbon concentrations in sediments for the particular time interval.

Taking into consideration that sedimentation rates were relatively low in the most Pshekhian basin and sediment thickness did not exceed 40–60 m in the studied areas, it is obvious that the presence of reducing environments favored the accumulation of elevated concentrations of OM, which was probably resistant to degradation. This supports the earlier conclusion (*Neftematerinskie...*, 1966). The organic matter was, however, significantly degraded that is evident from relatively low HI values.

This conclusion conflicts with an assumption (Lallier-Verges *et al.*, 1993) that the loss of the low-resistant part of phytoplankton OM in the course of sulfate reduction results in the selective accumulation of biore-resistant constituents, which are characterized by high hydrogen concentrations (in kerogen). The increased OM concentrations in the Pshekhian sediments accompanied by elevated HI values and higher HC potential can be related to the accelerated influx of phytoplankton-produced organic matter. The presence of reactive Fe could also play a certain role in this process. It is known that under Fe excess (relative to H_2S), hydrogen sulfide formed during sulfate reduction react with Fe, and pyrite is formed. More intense influx of phytoplankton-related, easily accessible OM will favor, all other parameters being equal, the acceleration of sulfate reduction. In this case, if the Fe content appears to be insufficient for pyrite formation, the excessive hydrogen sulfide commences to react with lipid components of organic matter. Organosulfurous compounds formed in this manner are resistant with regard to bacterial degradation and characterized by the elevated HC potential (Lallier-Verges *et al.*, 1997).

The highest OM contents are recorded in sediments that were accumulated in the first half of the Solenovian time (the second half of the Early Oligocene). The synchronous OM enrichment in sediments above the Ostracoda Bed is most probably related to this event.

The formation of this bed, "exotic" for Maikop deposits, was related to sharp changes in the hydrological regime of the basin, whose nature remains unclear so far. Based on the study of sections in Northern Ustyurt and the Aral region marking the marginal zones of the sea basin, Voznesenskii (1978) concluded that the maximum regression corresponded to the beginning of the Solenovian time. This coincides with the beginning of warming and increased seasonal climatic contrast (Oligocene Optimum), which is confirmed by the higher content of pollen of thermophilous seed plants, including representatives of evergreen forms, and a higher role of *Quercus gracilis* and *Q. gaciliformis* pollen more characteristic of sediments of the second half of the Eocene in the spores and pollen spectrum.

In the opinion of some researchers (Zhizhchenko, 1969; Popov *et al.*, 1993a; Popov and Stolyarov, 1997), the Parathetys lost its connection with the World Ocean

at the beginning of the Solenovian time. The water salinity in the basin did not exceed 10–12‰ owing to the fresh water influx. According to the other point of view (Muzylev *et al.*, 1992; Akhmet'ev and Zaporozhets, 1996; Zaporozhets, 1998b), the Solenovian basin preserved some connection with the World Ocean, although the water exchange between them was significantly impeded. In this case, Muzylev *et al.* (1992) relate freshening of sea water in the Solenovian time to a presumed general lowered salinity of the World Ocean. The restoration of the water exchange with open ocean in the second half of the Solenovian time promoted the influx of heavier sea waters into the freshened basin and their stratification (Voronina and Popov, 1987). Sediments accumulated at that time are barren of mollusks (Popov *et al.*, 1993b). Nonetheless, the occurrence of fucoids as well as the phytoplankton composition suggest that only bottom waters were oxygen-deficient in the most part of the basin (Popov *et al.*, 1993b; Akhmet'ev and Zaporozhets, 1996).

After comparing the succession of geological events, it can be assumed, with sufficient confidence, that the formation of Solenovian organic-rich sediments was controlled by the same mechanism that was responsible for the formation of Black Sea sapropels. After studying the evolution of geochemical conditions in the Black Sea, Strakhov (1971, p. 3) noted that "enrichment of Black Sea sediments with organic matter chronologically coincides with the moment of penetration of Mediterranean waters into the Black Sea basin and with the hydrogen sulfide contamination of waters. Some time later, TOC accumulation was sharply reduced, although H_2S contamination continued to exist and was probably even more intense than during the Old Black Sea time." As for the penetration of Mediterranean waters, its possibility was assumed earlier (Andrusov, 1905; Arkhangel'skii and Strakhov, 1932, 1938). Strakhov proposed the following mechanism of this event. Deep waters of the Neoeuxinian basin accumulated biogenic elements similarly to deep water horizons of the modern Caspian Sea. The sinking of heavy Mediterranean waters to the basin bottom resulted in the upward squeezing out of waters with the elevated content of nutrients (phosphates, nitrates, silica). Additional nutrients entered the photosynthesis zone and provoked a sharp increase in the phytoplankton productivity. When nutrient reserves were exhausted, the latter was significantly reduced, and Old Black Sea sediments rich in OM were replaced by modern mud with the significantly lower OM content, although hydrogen sulfide contamination of bottom waters continued and evidently became even stronger (Strakhov, 1976).

The impact of the high primary biological production of the sapropel formation in the Black Sea was also emphasized by other researchers (Sorokin, 1982; Glenn and Arthur, 1985; Calvert, 1987, 1990; Pedersen and Calvert, 1991), who assumed an existence of anaerobic conditions during the accumulation of organic-rich

sapropel mud in the Black Sea. Nevertheless, later some of them (Calvert and Pedersen, 1993) again stressed that high bioproductivity was a main factor responsible for its formation. However, the presence of a specific biological marker in the Old Black Sea sediments, i.e., *isorenieraten* (Repeta, 1993; Damste *et al.*, 1993), a carotenoid characteristic of photosynthetic bacteria *Chlorobium* (although in an insignificant amount as compared with that in overlying modern sediments), most likely indicates an unstable anoxic regime.

The study of pyrite framboids from Holocene sediments of the Black Sea revealed their identity in the Old Black Sea and Recent sediments and a sharp difference in pyrite framboid dimensions from fresh-water Neoeuxinian sediments (Wilkin *et al.*, 1997). Based on these features, Wilkin *et al.* concluded that organic-rich sediments of the Old Black Sea and organic-poor sediments of the late Black Sea were accumulated under similar conditions of the H₂S contamination.

According to Middelburg *et al.*, (1991), the mechanism, absolutely similar to that proposed by Strakhov, was responsible for the accumulation of Holocene OM-rich sediments in the Kay Bay (Indonesia). The transgression that followed last glaciation resulted in the restoration of the exchange between this formerly isolated fresh-water basin and World Ocean. Similarly to the Black Sea, the formation of the organic-rich section chronologically coincided with the initiation of the water exchange. Thus, our data support the earlier conclusion (Middelburg *et al.*, 1991) that epicontinental basin sediments, accumulated at the initial stage of the renewed water exchange with the World Ocean during transgressive phases, represent a specific object from the point of view of the petroleum geology.

There is also a different viewpoint on the sapropel formation in the Black Sea. Deuser (1974) proposed a model which is principally different from that considered by Strakhov. According to this model, water stratification owing to the sinking of heavy Mediterranean waters to the bottom and formation of stagnant anaerobic conditions were responsible for the accumulation of organic-rich sediments in the Black Sea. In this case, the lower TOC content in overlying modern sediments could be related to their dilution by the carbonate material (Wignall, 1994). The analysis of many publications reveals that most authors prefer this model. However, it is impossible to explain, using the Deuser's model, the accumulation of Solenovian organic-rich sediments in the Maikopian basin.

The beginning of the Late Oligocene was marked by the fast and significant eustatic sealevel fall (Haq *et al.*, 1987). The lowered base level of erosion resulted in a sharp activation of the paleo-Don River (Nedumov, 1994) and, correspondingly, in the influx of a large amount of the terrigenous, largely sandy material into the Maikopian basin. Its provenance was located in the modern northern part of the Caspian Sea (Nedumov,

1994). Beginning from that time, vast depressions of the Eastern Ciscaucasia and Central Caspian Sea were intensely filled with sediments (Stolyarov and Ivleva, 1993; Popov *et al.*, 1993a). The water exchange with the World Ocean became free. Simultaneously, the saline regime of the surface water lost its stability and varied from 25 to 5–10‰ in the northeastern part of the basin (Popov *et al.*, 1993a). The basin bottom topography probably favored the preservation of water stratification and stagnant conditions in its deeper parts. Most thin sections of Upper Oligocene rocks continue to show a thin undisturbed lamination (in some more silty varieties, lamination is less distinct). The benthic fauna occurs exclusively in relevant rocks of shallow-water coastal origin. In the opinion of Popov and Stolyarov (1997), the Late Oligocene Maikopian basin represented an analogue of the modern Black Sea. Uranium deposits of Mangyshlak and Ergeni are related to sediments accumulated in this basin (Stolyarov and Ivleva, 1995; Stolyarov and Kochenov, 1995). The preservation of stagnant conditions during the considered period of the basin history is also evident from the composition of green algae and acritarchs studied by Akhmet'ev and Zaporozhets (Popov *et al.*, 1993a), elevated values of the Mo/Mn ratio, which represents the stagnation coefficient (Kholodov and Nedumov, 1993), and also from other criteria indicative of H₂S contamination of the basin (Kholodov and Nedumov, 1991; Kholodov and Paul, 1995).

All of the aforesaid indicate that the lowered HC potential of Upper Oligocene Maikop rocks is controlled by several factors, whose role in different areas depended on local paleogeographic and hydrodynamic conditions: (1) the OM loss during the intense bacterial sulfate reduction; (2) the progressively increasing influence of allochthonous continental organic matter; (3) significant dilution of OM by the terrigenous material, which, in addition, provided an excess of Fe. Based on mineralogical and geochemical features of Maikop rocks, Nedumov (1994) concluded that in the late Maikopian time, the influence of the terrigenous material transported from the platform significantly increased in the Central Ciscaucasia region. Besides, the substantial increase in the content of palynomorphs and preserved fragments of higher plants in the Upper Oligocene–Lower Miocene sediments of the Belaya River indicates, with sufficient confidence, an increased influence of the Caucasian archipelago on sedimentation in the considered region.

CONCLUSION

The obtained data show that, despite the elevated average values of the organic carbon content, Maikop sediments of the Ciscaucasia region are generally characterized by the medium, not high as is usually thought, HC potential.

Within the entire Maikop sequence, the elevated OM concentrations are characteristic of Lower Oli-

gocene rocks. Relatively low values of HI commonly indicate significant degradation of organic matter. Elevated OM concentrations in the Lower Oligocene rocks accompanied by the increased HI values as well as by higher HC potential are probably related to the reinforced influx of OM into sediments.

The synchronous OM-enrichment level, which is quite unusual for the Maikop sediments, is noted in the second half of the Early Oligocene. Chronologically, this enrichment coincides with the period of restored connection of the Maikopian basin with the World Ocean at the beginning of the transgressive stage. We believe that this enrichment resulted from bioproductivity outburst, which is consistent with the model proposed by Strakhov (1971) to explain the accumulation of Old Black Sea sapropels.

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Mesozoic Carbonaceous Clayey Formations of the Central Russian Plate: The Problem of Their Ore Potential

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Abstract—Polyfacial organic-rich clayey horizons in Jurassic and Cretaceous sections of the central Russian Plate exhibit a similarity to the domanik beds. These horizons are divided into three major groups of facies. The locally distributed continental facies (group 1) is characterized by the development of uranium and REE mineralization. The lagoon-marine facies (group 2) is similar in lithochemical specialization to the black shale horizon hosting multicomponent ores in southern China. The deep-sea facies (group 3) have been poorly studied, so their metal potential remains unclear. A complex of forecasting and prospecting criteria has been elaborated for revealing the metalliferous facies.

Among diverse potentially ore-bearing geologic formations in covers of ancient platforms, of particular interest regarding the metal potential are specific polyfacial carbonaceous clayey formations characterized by dark to black color, small thickness, and continuous areal distribution. They are composed of continental or marine (planktonic) organic-rich silty-clayey rocks with sulfides and siderite. Subordinate interlayers of black bituminous limestones, marls, and siliceous rocks are present as well. Parts of the formations, that were accumulated near ancient shore zones, as well as the basal members, are often strongly enriched in phosphorus.

The composition of such formations is dominated by relatively deep-sea facies (the domanik facies, named after the Domanik River in the southern Timan Ridge), which are considered to be the major oil-generating rocks. Of a subordinate significance are lagoonal-marine facies accumulated at shallower depths. Sometimes, continental facies are encountered, which are represented by lacustrine-boggy and mixed sediments of dammed paleovalleys on coastal lowlands. This facial complex dominated by the domanik facies proper allows us to identify the rocks under consideration as domanikoid rock. They are characterized by the occurrence of shallow-water, sometimes continental, rocks with distinct boundaries. Such a relationship is evidence for a sharp change in the sedimentation conditions.

The compositional peculiarities of the domanikoid formations and the character of their lower boundaries suggest a rapid, uncompensated subsidence of the corresponding platformal blocks during their accumulation. Such subsidences of peripheral segments of the platforms are related to downwarping within their adjacent mobile belts and, therefore, can be assigned to the resonance-type processes (according to Yu.M. Push-

charovsky). The nature of rapid, short-term subsidences of inner segments of the platforms (synclises and depressions) is explained by sharp changes in the properties of deep-seated crustal horizons, e.g., by an increase in weight of the basaltic layer owing to the phase transition of basalt into denser eclogite above areas of upwelling of the anomalously heated mantle (Artyushkov and Beer, 1986).

The depth of marine (domanik) rock formation can be determined based on geological data and a complex of fossil organic remains. The most reliable depth determinations for paleobasins are those based on the thickness of deltaic sandy-silty clinoforms covering the domanik horizons. The Upper Jurassic Bazhenovo Formation of the sedimentary cover of the West Siberian Plate represents a typical domanikoid formation. Judging from the thickness of Lower Cretaceous clinoforms (Kunin, 1983; Mikhailov and Shlezinger, 1989), this sequence was deposited at a depth of 300–500 m. It most likely seems that this is the maximum depth of formation for platform domanik rocks. The significant depth is also confirmed by peculiarities of the fossil organic remains. Indicative is an almost entire absence of benthic forms—brachiopods, corals, and pelecypods—with a predominance of freely swimming cephalopods and floating foraminifers and radiolarians here. The minimum depth of formation for marine domanik horizons, which are commonly thin, but distributed over vast areas, is 35–40 m. This is the depth of the roiling action of storm waves within open sea areas (Antsyferov and Kos'yan, 1986). In the case of shallower depths in the vast basins, the black clays and muds would inevitably be mixed with underlying sands or carbonate muds during strong storms.

The carbonaceous clayey formations under consideration are encountered in sections of platform covers, beginning primarily from the Upper Precambrian

(Malga Formation of Siberia), although they are occasionally noted even in Lower Precambrian protoplatformal covers (e.g., shungites of the Zaonega Formation in Karelia). These formations are much wider distributed in Phanerozoic covers. For example, they are found in the Lower Cambrian along eastern margins of the ancient Siberian and South Chinese epibaikalian platforms, in the Middle and Upper Cambrian on the western slope of the Baltic Shield in Sweden, in the Lower and Middle Ordovician of the Baltic region; in the Upper Devonian of the Timan Ridge and eastern Russian Plate (classic regions of domanik facies); in the Upper Devonian and mid-Carboniferous of the eastern North American Plate; and in the Upper Jurassic of the West Siberian Plate (the above-mentioned Bazhenovo Formation).

Several carbonaceous clayey horizons in Jurassic and Cretaceous sections of the central Russian Plate, which likely belong to this formational type, are discussed in this work.

The metal potential of many of the above-listed carbonaceous clayey formations is suggested by elevated contents of several ore components, which are often two or three orders of magnitude higher than the background levels and, sometimes, even reach the ore-grade concentrations. In this respect, of exceptional interest are stratiform, multicomponent (Mo- and Ni-rich) ore deposits that were recently discovered in the South Chinese Platform cover. Since these ore deposits represent first commercial-grade objects within formations of the type under consideration, it is expedient to dwell on peculiarities of their structure and ore composition.

According to data of Coveney and Nancheng (1991) and Konkin *et al.* (1993), these ore deposits are confined to a continuous basal horizon of the Lower Cambrian terrigenous-carbonate series discordantly overlying the Vendian carbonate sequence. The basal horizon is composed of black, organic-rich shales and is considered by us as a carbonaceous clayey formation. The horizon represents a thin (~10 m), wide (150–200 km) and long (up to 2000 km) zone. It outlines a deep shelf that existed during its formation. The overlying Devonian and Lower Carboniferous rock sequences with a total thickness of up to 4–5 km are represented by shallow-water terrigenous-carbonate rocks (Il'in, 1986).

The basement of the horizon incorporates a discontinuous lenticular layer of gritstones with grains primarily represented by poorly rounded phosphorite clasts. Upward the section, the gritstones are abruptly replaced by black claystones and shales. In the lower section of the horizon, the clayey rocks are strongly enriched in OM (from 5–7 to 18–20%). Therefore, the local inhabitants call them "hard coal" and use them for heating. In addition, these rocks are enriched in phosphorus (Il'in, 1986). It is this part of the section that accommodates the ore mineralization. In the middle and upper sections of the horizon, the OM and P con-

tents are decreased and no ore mineralization has been noted.

Black shales in the ore-bearing section of the horizon contain thin (2–30 cm) lenticular ore bands, which contain sulfide mineral fragments and concretions (90%) and a subordinate amount of phosphatic and carbonate nodules. The cement consists of sulfides, carbonate phosphates, quartz, carbonates, and siliceous material. The major ore minerals are represented by pyrite, millerite, bravoite, gersdorffite, molybdenite, and jordisite. The auxiliary ore minerals are sphalerite and chalcopyrite. Pentlandite, tennantite, violarite, uraninite, timmanite, and small particles of native gold are sporadically encountered. Pt and Pd are present in timmanite. The U- and Th-containing phosphates are minor. The bands with multicomponent ores contain the following metals: Mo 4%, Ni 2–7%, Zn 2%, Au 0.7 g/t, Ag 50.0 g/t, Pt 0.3–0.4 g/t, Pd 0.4 g/t, Ir 0.03 g/t, and Os 0.17–0.50 g/t.

Organic matter in the ore bands is represented by graphite and pyrobitumen (average ~10%). Microfossils (sponge spicules and remains of cyanobacteria and algae) were revealed in OM patches. Separate bands contain OM segregations that are partly replaced by sulfides and represent cyanobacterial mats. Such bodies are indicators of relatively shallow-water conditions that episodically appeared due to oscillating tectonic movements in the beginning of general subsidences.

Among other platformal formations of the type under consideration, where elevated contents of various metals have been revealed, the mid-Paleozoic rocks in the North American Platform cover should be noted. The eastern segment of this platform includes U- and V-bearing black shales (Chattanooga Shale) that are assigned to the upper Devonian–Lower Carboniferous. Within this same area, upward the section of the platform cover, at the boundary between the Middle and Upper Carboniferous (the mid-Pennsylvanian), black shales (Mecca Quarry Shale) and their stratigraphic counterparts occur. Along with U, they contain significant (two orders of magnitude higher than Clarke values) concentrations of Mo, V, Cd, Se, and Sb; they also contain PGE. The Mecca Quarry Shale and its analogues constitute a thin (< 1 m), but highly continuous marker horizon within the Midcontinent, i.e., the central and eastern segment of the Mississippian Plate. Nevertheless, the compositional distinction of this bed from the under- and overlying shallow-water gray-colored rocks allows to identify it as a specific carbonaceous clayey formation. Coveney *et al.* (1987) studied the vast (no less than 400 by 1300 km) sedimentary basin, within which this black shale horizon is developed and revealed an important relationship between the metal contents and continental OM accumulated in clayey sediments near the eastern shore of the paleobasin. The Mo and V contents of the sediments are more than 0.1 wt % in the shore zone. However, in the major part of the paleobasin, OM in pelites is of primarily

marine, planktonic origin, and the metal content in shales is decreased by one or two orders of magnitude.

The presented brief review allows us to conclude that platformal carbonaceous clayey formations have a good multicomponent ore potential.

Below, we describe polyfacial domanikoid horizons in Jurassic and Cretaceous sections of the central Russian Plate. Until the present time, rocks of these sections were traditionally considered as shallow-water formations. Nobody correlated them with the domanik beds. These horizons were not examined for the metal potential, although geologists of the former PGO Tsentrgеologiya had revealed certain U and REE occurrences, some of which were accompanied by Au and Ag mineralization. The origin of these objects was explained by their confinement to hidden fractures in the platform cover or to paleovalleys, assuming an infiltration-type genesis of the ore mineralization. No significance was attached to the relationship between the elevated background metal content and the formational type of rocks.

At the same time, the above-mentioned data clearly evidence an existence of such a relationship. Therefore, we attempted to estimate the ore potential of Jurassic and Cretaceous domanikoid formations. Among Mesozoic shallow-water gray-colored silty-sandy rocks, black siltstones and clays constitute six major horizons consisting of carbonaceous clayey formations (Konstantinovskii *et al.*, 1996) (Fig. 1).

The lower, mid-Jurassic (Bajocian–Bathonian) formation, according to data of S.L. Breslav, V.A. Zhukov, S.I. Gol'ts and other researchers of the PGO Tsentrgеologiya, is fragmentarily distributed on the northern and eastern slopes of the Voronezh Antecline, on the southern limb of the Moscow Syncline, and on the northern limb of the Ul'yanovsk–Saratov Syncline, under a cover of Jurassic and Cretaceous marine sediments. Rocks of this formation are assigned to the Bajocian in the east and to the Bathonian in the west. It sharply differs from the overlying carbonaceous clay by the continental genesis and is represented by monotonous lacustrine–boggy and floodplain facies. Their accumulation in small depressions and pre-Middle Jurassic paleovalleys could only be realized under stagnant conditions. The rapid subsidence of land subjected to erosion and damming of rivers were responsible for stagnant conditions. The deposits are represented by gray to black organic-rich clays and silts. These rocks contain disseminated plant detritus as well as sporadic remains of coalified wood and lenses of brown coals. A characteristic feature of these rocks is the presence of authigenic sulfides (primarily, pyrite and marcasite), which form layered impregnation and chains of nodules, suggesting a reductive sedimentation environment. The thickness depends on the depth of the paleovalleys and varies from 20–30 m in general to 50–70 m in deep mouths of tributary valleys and ancient karstic subsidences. Channel alluvium deposited at the stage

of downcutting of the valleys at the Early–Middle Jurassic transitional time, is extremely thin (no more than 1–3 m). It is preserved as separated lenses under dark-colored clays on bedrock of karstified Devonian and Carboniferous carbonate rocks. The alluvium is represented by lenses of clayey sands and allochthonous products of erosion of the pre-Middle Jurassic weathering crust, brown iron ores and kaolinic clays. The sandy layer and the basal layer of dark gray clays, which overlie the carbonate substrate, include rubble, fragments, and, sometimes, large lumps of the local, predominantly silicified limestones and dolomites. It is likely that this coarse-clastic material represents residual products of rewashing of ancient rockslides (from the paleovalley slopes) and gully proluvium cones.

In contrast to the mid-Jurassic continental rocks, the overlying Upper Jurassic and Lower Cretaceous carbonaceous clayey formations are encountered as mantle-type bodies alternating with shallow-sea (glauconite-containing) and, less frequently, continental gray-colored silty-sandy sediments. They fill vast sedimentary basins formed in the Late Jurassic, including the superimposed Ul'yanovsk–Saratov Syncline overlapping the buried Tokmovo Arch; the Moscow–Galich Depression inheriting in part the structure of the Paleozoic Moscow Syncline; and the Shilovo–Vladimir and Moscow–Oka troughs formed above the Riphean Moscow Graben and the northwestern end of the Pachelma Aulacogen, overlapped by a thick Paleozoic cover.

We have distinguished the following carbonaceous clayey formations (from the bottom to the top of the section): the Oxfordian–Kimmeridgian formation, the Lower–Middle Volgian formation, the Hauterivian–Lower Barremian formation, the Aptian formation (in the upper section among continental quartz sands), and the terminal Albian formation.

The common peculiarities of these formations are as follows: (1) A wide distribution and subaqueous genesis (*Geologiya...*, 1967; Sazonova, 1958; Sazonov *et al.*, 1964; Turov, 1998). An exception can be represented only by the most ancient fragments of basal layers confined to hollows in the basement, presumably represented by continental clays analogous to the Bajocian–Bathonian ones. (2) Regular compositional changes in the sediments from the west (Moscow region) to the east (central Volga region), expressed in a higher enrichment in nodular phosphorites of the western sections and in an appearance of interlayers of marls and siliceous rocks in the east. (3) An eastward increase in the thickness of the carbonaceous clayey formations. Some of them, e.g., the Albian formation and the thickest Hauterivian–Lower Barremian one, are even completely wedged out in the west, in the Moscow region. (4) A scarcity and specific composition of fossil fauna in the formations. This fauna is almost exclusively represented by freely swimming cephalopods (ammonites and belemnites), which are more inherent in deep-shelf sediments than to shallow-water near-

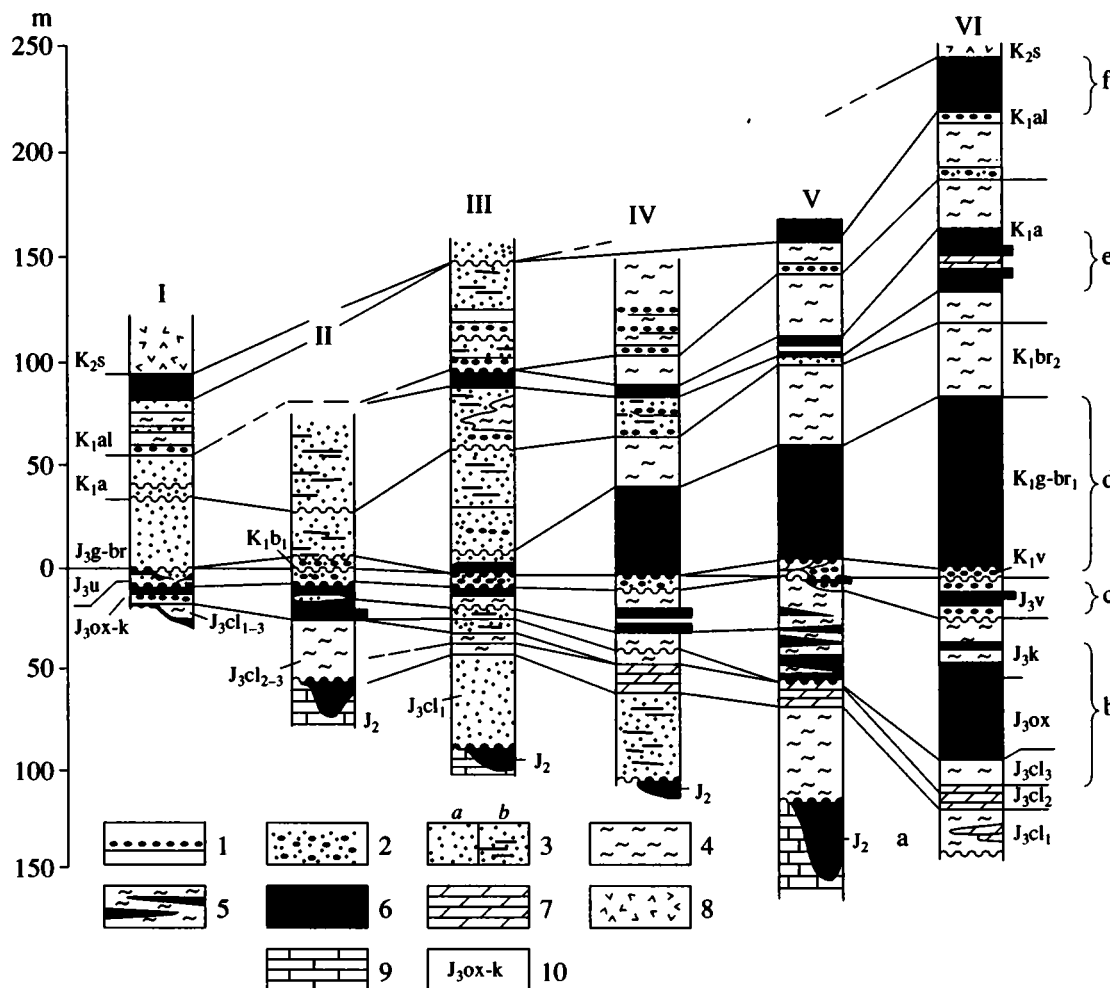


Fig. 1. Carbonaceous clayey horizons in Jurassic and Cretaceous sections in the central Russian Plate. Horizons: (a) mid-Jurassic (Bajocian–Bathonian), (b) Oxfordian–Kimmeridgian, (c) Early–Middle Volgian, (d) Hauterivian–Barremian, (e) Aptian, and (f) Albian. Reference sections: (I) southern end of the Moscow Syncline (the city of Moscow and the southern Moscow region); (II) Shilovo–Vladimir Depression (the eastern segment of the Moscow–Oka Depression); (III) western limb of the Ul'yanovsk–Saratov Syncline (the Murom–Lomov Depression); (IV) central segment of the Ul'yanovsk–Saratov Syncline in the vicinities of the town of Penza, settlements of Mokshany and Rangilei, and upper reaches of the P'yana River; (V) central segment of the Ul'yanovsk–Saratov Syncline in the vicinity of the Settlement of Prudy, and in the upper and medium reaches of the Sura River; (VI) eastern limb of the Ul'yanovsk–Saratov Syncline in the vicinities of the towns of Ul'yanovsk and Syzran.

Lithologic characteristics: (1) nodular phosphorites and phosphoritic conglomerates; (2) quartz–glaucinite sands and sandstones with phosphorites (reduced layers); (3) oligomictic and quartzose sands and sandstones: (a) well washed and (b) clayey varieties; (4) gray silty and calcareous clays with marly concretions, phosphorites, and siderite; (5) alternation of gray and black clays with dark sands containing pyrite and marcasite and interlayers of silicified varieties and combustible shales (ledges in the right sides of the columns); (6) carbonaceous clayey horizons; (7) marls; (8) tripolis and opokas, interstratified with quartzose sands; (9) limestones and dolomites of the Carboniferous, constituting the basement of the Mesozoic complex; and (10) stratigraphic subdivision indices for the Jurassic and Cretaceous deposits.

shore ones. According to the latest data, the typical Albian formation is composed of black silty clay layers, 10–15 m (rarely up to 30 m) thick, accumulated at a depth of 90–100 m. This conclusion is supported by the presence of peculiar planktonic foraminifers and radiolarians (Alekseev *et al.*, 1996). It is likely that compositionally analogous aleurolites in the thick eastern sections of the Upper Jurassic and Lower Cretaceous formations were characterized by similar depths of sedimentation.

The thin western sections of the Oxfordian–Kimmeridgian and Lower–Middle Volgian formations of the Upper Jurassic were probably formed in shallower, lagoonal–marine conditions of sedimentation. This assumption is confirmed, first, by their proximity to the western flank of the paleobasin and, second, by an enrichment of the sediments in nodular phosphorites, which are indicators of shallow depths. In the Shchelkovo and S'yanyovo quarries in the Moscow region, phosphorites are found as chainlike conformable interlayers

Comparative characteristics of spectral data on Upper Jurassic carbonaceous clayey deposits from the Moscow Syncline and for more ancient rocks from this same area

Rocks	Elements and their average contents, %				
	V	Ni	Co	Zn	Mo
Silty-clayey rocks of the Upper Vendian and the Middle and Upper Devonian (7 analyses)	0.01	0.0016	0.001	0.0035	0.00007
Carbonate rocks of the Upper Carboniferous (4 analyses)	0.002	0.0015	0.0005	—	0.00005
Carbonaceous clayey rocks of the Upper Jurassic (7 analyses)	0.005	0.03	0.005	0.035	0.0002
Carbonaceous claystone from the Upper Jurassic basal horizon (1 analysis)	0.006	0.2	0.1	0.15	0.00008
Marcasite concretions from the Upper Jurassic carbonaceous clayey rocks (2 analyses)	0.001	0.025	0.0008	—	0.0008

in black shales with vertical intervals of 0.3–0.7 m. Two such interlayers have been sampled in detail for studying their metal potential.

Upper Jurassic and Lower Cretaceous formations display three compositional groups of facies: (a) the continental facies in paleovalleys and small depressions on the pre-Middle Jurassic regional unconformity surface; (b) the overlying lagoonal-marine facies which are anomalously enriched in P and developed in near-shore parts of the Late Jurassic basin, as is seen on an example of the Moscow region; and (c) the marine facies accumulated at relatively great depths and represented by sediments of the eastern sections as well as by black clays of the terminal Albian in the northern Moscow region and Vladimir province. The above-characterized facial groups correspond to respective sections of the carbonaceous clayey formations (lateral and vertical series).

It is important to note that, in terms of the P content, sediments of western sections, which represent the lagoonal-marine facies group, are similar to Lower Cambrian ore-bearing P-rich black shales of the South Chinese Platform. It is possible that the presence of high P contents in carbonaceous clayey sediments can serve as a prognostic criterion for the metal potential. This problem requires further investigations.

Rare U and REE occurrences, sometimes with Au and Ag, have been recently revealed in the Jurassic and Cretaceous black aleuropelites of the central Russian Plate.

The most interesting is the Kurlei REE–U occurrence discovered in continental mid-Jurassic silty-clayey rocks as a result of works headed by F.S. Mudarisov (Srednevolzhsk Geological Exploration Expedition). The ore-bearing sediments fill ramified paleovalleys in the northern Ul'yanovsk–Saratov Syncline and are overlain by Bathonian marine sediments and Neogene continental sediments. Drilling works revealed that most radioactive were mid-Jurassic (Bajocian) basal horizons of the dark-colored organic-rich silts and clays in paleovalleys cutting Upper Carboniferous carbonate rocks. The depth of the paleovalleys

varies from 25 to 35 m. Ore-bearing sediments are located at a depth of no more than 70 m from the ground surface. Along with ordinary uranium ores, rich ores with an U content of up to 0.54% and thickness of 0.3 m were revealed in the basal siltstones and clays. They occur in very deep areas, where tributary valleys are connected with the major valley. Thus, the U mineralization clearly controlled by paleogeomorphologic, stratigraphic, and lithologic factors. The U-bearing horizons include a number of geochemical anomalies of REE, including Sc (200–260 ppm), Ce (up to 2000 ppm), Nd (150 ppm), La (600 ppm), and Y (300 ppm). Additional components include Au in the basal horizons (0.0n–0.1n, maximum 30.0 g/t (!) in a 0.1-m-thick, U-rich interval) and Ag (up to 3.0 g/t). Other elements, such as Mo, Zn, and Cu are universally present in association with U, precious metals, and REE within the basal horizons and, in less amounts, upward the section.

With respect to the specified metal association and, primarily, to their quantitative relationships, the Kurlei ore occurrence differs from ore-bearing marine carbonaceous clayey (domanikoid) formations of other regions, including the South Chinese Platform. This ore occurrence is marked by the abundance of U and a wide range of REE, while P is practically absent. The role of Mo, Zn, and Cu here is relatively low.

We have conducted a preliminary sampling of domanikoid formations in the northern and eastern parts of the Moscow region. In black silty clays from the Upper Jurassic (Oxfordian–Kimmeridgian and Lower–Middle Volgian) relatively shallow-water formations, geochemical anomalies of Ni, Mo, Co, Cu, and Zn have been revealed. It should be noted that these metals are practically missing from the continental mid-Jurassic formation of the Russian Plate, but are characteristic for multicomponent ores in the Lower Cambrian black shales of the South Chinese Platform (table). The presented table shows a set of spectrometric data for the same elements in other rock sequences of the platform cover in the central Russian Plate. It is clearly seen that the Upper Jurassic carbonaceous formations are enriched in the specified metals to a far

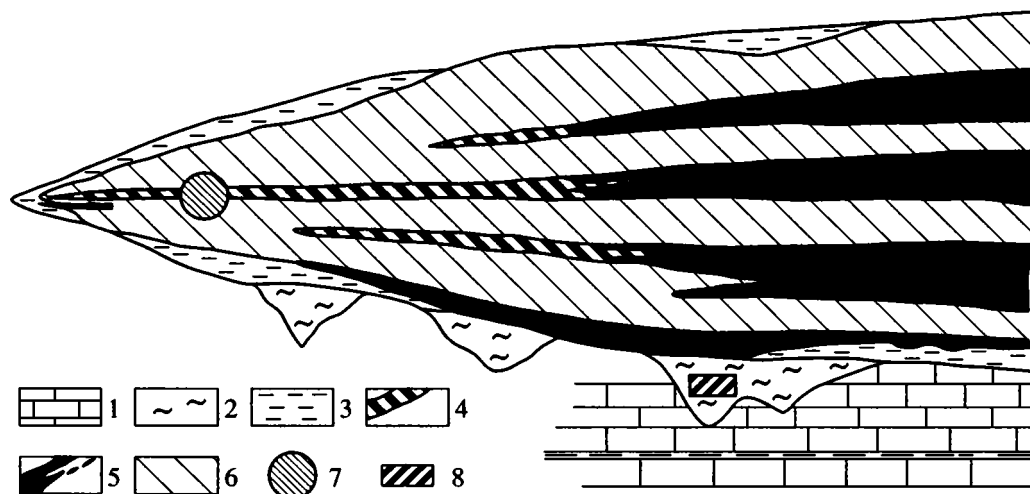


Fig. 2. Sketch section showing the principal structure of the Mesozoic clayey-terrigenous complex of the central Russian Plate, hosting carbonaceous clayey (domanikoid) formations. (1) Basement rocks; facies groups of carbonaceous clayey formations: (2) lacustrine-boggy and alluvial (predominantly floodplain), (3) mixed lacustrine-boggy and lagoonal, (4) phosphorite-enriched lagoonal-marine, (5) deep-sea facies; (6) gray-colored shallow-water and continental silty-sandy formations; ore occurrences: (7) multicomponent (V, Ni, Co, Zn, Mo, and P), (8) REE-U (in places, with Au and Ag).

greater extent, as compared to organic-depleted clayey horizons in the Upper Vendian, Middle-Upper Devonian, and Upper Carboniferous sections. It is interesting to note that the most metal-enriched unit here is represented by a basal, thin (1 cm) clayey siltstone band that begins the Oxfordian-Kimmeridgian section, where it discordantly overlies the karstified surface of the Upper Carboniferous light-colored limestones. As is seen from table, anomalously high Co, Ni, and Zn concentrations have been revealed in this band.

The lithochemical specialization of the comparatively deep-sea domanikoid formations of the Upper Jurassic and Lower Cretaceous in the eastern sections (the central Volga River) remains to be studied. By analogy with far deeper (about 2 km) marine metalliferous muds of the Black Sea (Pilipchuk and Volkov, 1966), it can be supposed that the domanikoid formations are enriched in Mo, although in the case of a predominance of marine (planktonic) OM, the Mo content will most likely be relatively low.

CONCLUSION

(1) Polyfacial dark-colored silty-clayey horizons in Middle-Upper Jurassic and Lower Cretaceous sections of the central Russian Plate can be distinguished as carbonaceous clayey (domanikoid) formations. In terms of the composition and the accumulation conditions, they have much in common with horizons of black aleuropelites, which are distributed in other regions and belong to the same formational type.

(2) Facies incorporated into the formations considered are divided into three major facial groups: (a) basal, continental facies confined to paleovalleys and depressions; (b) lagoonal-marine facies; and (c) marine,

relatively deep-water, domanik facies proper. The groups make up vertically and laterally arranged series and, based on preliminary data, are different from each other in the lithochemical specialization (Fig. 2). Continental facies are characterized by the presence of U mineralization with REE. Lagoon-marine facies, enriched in P_2O_5 , are similar in the lithochemical specialization to the ore-bearing horizon of southern China. The metal potential of the marine, relatively deep-water facies, is poorly studied until the present time.

(3) The major peculiarity that distinguishes the Jurassic and Cretaceous domanikoid formations of the central Russian Plate from ore-bearing carbonaceous clayey horizons in the sedimentary covers of other platforms consists in a small (no more than 200–300 m) amplitude of their postsedimentary subsidence. In contrast, the ore-bearing domanik horizon of the South Chinese Platform, judging from the thickness of the overlying cover rock sequences, experienced a subsidence to a depth of no less than 4–5 km after its accumulation. This statement is also true for the Chattanooga and Mecca Quarry metalliferous black shales on the North American Platform. Since the depth of subsidence and related compositional transformations of OM-rich aleuropelites exert an effect on the metal concentration, the ore potential of the examined Jurassic and Cretaceous formations should be considered to be relatively low.

(4) Based on the above-presented materials, we have elaborated the following forecasting and prospecting criteria, which facilitate a discrimination between gray-colored clayey-terrigenous complexes like the Mesozoic one in the central Russian Plate and provide grounds for distinguishing the potentially ore-bearing

facies within them: (a) the presence of black carbonaceous clayey horizons (domanikoid formations) in the composition of the gray-colored complexes; (b) the presence of the above-mentioned facial groups (including the basal continental ones in paleovalleys) in the composition of the horizons; (c) the predominance of the continental-type OM, relative to the marine (planktonic) variety; (d) elevated P_2O_5 contents related to nodular and layered phosphorites and the presence of dispersed P; and (e) the presence of areal radioactive anomalies (the ore mineralization of the South Chinese type is confined to their flanks).

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H and O Isotopic Compositions of Layered Silicates in Metasomatites from the Gai Zn–Cu Massive Sulfide Deposit, Southern Urals

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Abstract—Substantial differences in isotopic compositions of micas and pyrophyllites from metasomatites related to various stages of the process that formed the giant Gai massive sulfide deposit have been established. The illite from the earliest and predominant chlorite–illite–quartz metasomatite is characterized by the least δD values of $-(50-85)\text{‰}$ and $\delta^{18}\text{O} = 7-11\text{‰}$. The pyrophyllite–quartz metasomatite as well as illite and pyrophyllite schists developed locally in the southern part of the deposit that likely correspond to the site of discharge of late geothermal paleosystem, contain pyrophyllite and illite with much higher values of $\delta D = -(25-45)\text{‰}$ and $\delta^{18}\text{O} = 4-9\text{‰}$. Local zones of illite–paragonite schist complete the mineral formation and are characterized by the transitional δD values of $-(30-55)\text{‰}$ and elevated $\delta^{18}\text{O}$ of $10-11\text{‰}$. The most plausible model of isotopic evolution in the hydrothermal system, with an initial temperature of mica formation at 250°C , assumes the mixing of transformed sea water with a magmatic (metamorphic) water at the initial stage when the background metasomatites and massive sulfide orebodies of the northern lode have been formed. Subsequently, after the burial of the northern lode beneath basaltic andesite flows, the repeated sea water invasions took place in the southern discharge site of the system. As a result, the pyrophyllite–quartz metasomatite was formed; the pyrophyllite and illite schists originated in tectonic compression zones. The interaction of this water with silicate rocks was completed by a formation of illite–paragonite schist. In general, the substantial contribution of sea water to the formation of metasomatic halo of the deposit casts no doubt.

The isotopic composition of micas from massive sulfide deposits and its genetic interpretation were comprehensively discussed for ore provinces of Canada, Japan, Cyprus, and other regions (Costa *et al.*, 1983; Franklin *et al.*, 1981; Hoy, 1993; Taylor, 1979; etc.). These investigations clarified the relationships between magmatic (metamorphic) and sea waters; the latter turned out to play the substantial role in the formation of metasomatic haloes. The available information on isotopic composition of micas from classic massive sulfide deposits of the Urals remained very restricted (Baranov *et al.*, 1989a, 1989b). We attempt to fill this gap by presenting the data about the unique Gai deposit.

The Gai Zn–Cu massive sulfide deposit is located in the southern Urals, 30 km north of the Orsk. The deposit is situated at the southern flank of the Baimak–Buribai zone within a large paleovolcanic edifice (D_1^1) rimmed by volcanomictic rocks of the Ultau Formation (D_2^2) (Borodaevskaya *et al.*, 1968; Medno-kolchedannye ..., 1988; Pshenichnyi, 1975; Zaikov *et al.*, 1989). The western part of the edifice is composed of

sodic rhyolite–basalt association related to the Baimak–Buribai Formation, and the eastern part is built up by basaltic andesites of the Irendyk Formation.

Numerous bodies of massive and disseminated sulfide ores are confined to the Central Fault and are concentrated within a common ore-bearing zone of background illite–quartz and illite–chlorite–quartz metasomatites. The total extent of the zone is 3700 m. The orebodies are grouped into three separate lodges: northern, central, and southern (Fig. 1).

The main volume of Cu and Cu–Zn ores is related to the largest northern lode (open pit 1), which comprises a series of closely-spaced roughly lenticular orebodies with a complicated history of recrystallization, which is completed by a bornite assemblage.

The central lode (open pin 3) mainly consists of pyrite ore surrounded by the illite–pyrophyllite–quartz and pyrophyllite–quartz metasomatites. The extended zone of pyrophyllite and illite–pyrophyllite schists is confined to the hanging wall of orebodies (Zaikov *et al.*, 1989).

The southern lode is represented by the least recrystallized Cu–Zn ore (open pit 2) localized in the background chlorite–illite–quartz metasomatite.

In general, the study of ores indicates that the central and southern lodes were formed after the burial of the northern lode beneath the seafloor. The ore-forming process was accompanied by a severe metasomatic alteration of the buried northern lode with an intense leaching of Cu from the lower part of lode (suggested by leaching voids left behind the chalcopyrite) and its redeposition in the upper part as a bornite ore.

Metasomatites at the Gai deposit, especially those located near orebodies, have a multistage history of their formation. The giant halo of the earliest chlorite–illite–quartz alteration resulted from the low-temperature (< 230–250°C) acid leaching. The local variety in the central lode (open pit 3) is represented by an illite–pyrophyllite–quartz rock. In shear zones, the above metasomatites are transformed into the mica schists. The schistose bodies, 1–15 m thick, are commonly located near lenses of massive sulfide ore and consist of low-temperature illite and the younger assemblage of paragonite, illite and K–Na mica. The illite rocks were studied in the southern lode, and the paragonite–illite rock is most abundant at upper levels of the northern lode. In shear zones, the pyrophyllite–quartz rock was replaced by a pyrophyllite schist. All types of metasomatites underwent the regional metamorphism of prehnite–pumpellyite facies (Borodaevskaya *et al.*, 1968) at a temperature below 300–350°C. More detailed information on metasomatites known at the Gai deposit was reported elsewhere (Grabezhev *et al.*, 1998a, 1998b).

Results of detailed electron diffractometry, X-ray, and microprobe studies of micas (analysts A.P. Zhukhlistov, G.V. Pal'gueva, and N.N. Kononkova) were taken into account in the interpretation of their isotopic composition. In the background chlorite–illite–quartz metasomatites, the pyrophyllite-bearing metasomatites, and the sericite schists, the mica is represented by a nonhydrated illite with an interlayer cation sum of 0.78–0.88 f.u. per 7 cations and with an extremely insignificant admixture of sodic micas, which are detected only by an oblique-ray electron diffractometry. In Na-bearing mica schist, the electron diffractometry reveals the assemblage of fine-flaky paragonite, K–Na-mica, and illite, the paragonite being predominant. All micas are related only to the 2M₁ modification.

On the basis of recent experimental results (Yates and Rosenberg, 1997 and others) and empirical data (Hunziker *et al.*, 1986; Korikovskiy *et al.*, 1995; McDowell and Elders, 1980), it may be assumed that the primary mica was represented by the hydrosericite or illite 1M transformed into illite 2M₁ in the course of prehnite–pumpellyite metamorphism at 300–350°C. According to experimental data, the temperature of the illite–muscovite transition exceeds 250–280°C (Yates and Rosenberg, 1997), and the temperature of the hydromica–illite transition is still lower. The homoge-

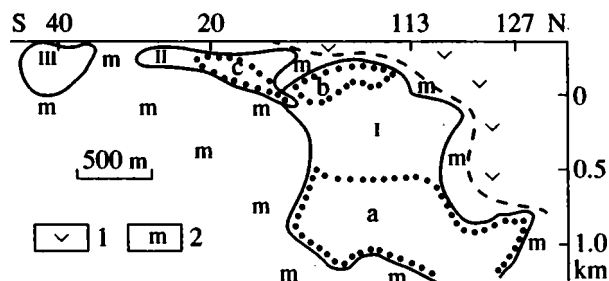


Fig. 1. Combined longitudinal vertical projection of ore zones and orebodies at the Gai deposit. (I) Volcanogenic sedimentary sequence; (2) background chlorite–illite–quartz metasomatite; (I) northern lode, open pit 1 including the system of eastern orebodies (a) and the axial lense (b); (II) central lode, open pit 3 including the pyrite orebody (c); (III) southern lode, open pit 2. Numbers of profiles where most of samples have been collected are shown above the line.

nization temperature of fluid inclusions in quartz and sphalerite commonly ranges from 200 to 300°C and occasionally reaches 380°C (data reported by G.N. Pshenichnyi, N.A. Andriyanova, and N.I. Nesterenko). The similar temperature range of gangue and ore mineral formation at other massive sulfide deposits of the Urals was reported by Karpukhina and Baranov (1995).

The location of analyzed samples is presented in table and Fig. 1. The samples of background metasomatites were collected from borehole cores at a depth of 1.2–1.7 km at the northern pinchout and in the central part of the northern lode. Metasomatites of other types were mainly taken from open pits from a depth down to 300 m.

The oxygen was extracted from minerals by means of the reaction with ClF₃ at 500°C, and then was converted into CO₂ by a reaction with graphite at 600–650°C. The determination of $\delta^{18}\text{O}$ was performed with a MI-1201B mass-spectrometer. The hydroxyl water was extracted from muscovite by a heating 1200°C after the preliminary treatment at 180°C, and then was decomposed on the metallic uranium at 800°C. The determination of δD was carried out with a GD-150 mass-spectrometer. The $\delta^{18}\text{O}$ and δD values are given in promilles relative to the SMOW standard. The accuracy of $\delta^{18}\text{O}$ and δD measurements was 0.2 and 2‰, respectively.

On the δD versus $\delta^{18}\text{O}$ diagram, the isotopic compositions of metasomatites are grouped into separate fields (Fig. 2). The illite from the background chlorite–illite–quartz rock in the central part of the northern lode in the open pit 1 and at the northern pinchout of the ore zone (Fig. 2, field I) is characterized by the least δD values of $-(50-85)\text{‰}$ and $\delta^{18}\text{O} = 7-11\text{‰}$. Illite–pyrophyllite–quartz, illite–quartz rocks, and illite and pyrophyllite schists replacing them in the central lode (Fig. 2, fields II and III) have a higher δD of $-(25-45)\text{‰}$. The mica from the zone of intense pyrophyllitization (open

Isotopic composition of layered silicates from the Gai deposit

Ord. no.	Sample no.	Rock	Mineral	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$, water	δD , water
Background chlorite-sericite-quartz metasomatite							
1	2390	Northern pinchout of the ore zone	Illite	7.8	-80	3.1	-44
2	294	The same	The same	7.0	-52	2.3	-16
3	159-89	Central part, profile 113	The same	7.5	-60	2.8	-24
4	203-89	The same	The same	7.1	-87	2.4	-51
5	152-89	The same	The same	10.5	-82	5.8	-46
6	246-89	The same	Hydroillite	8.5	-60	3.8	-24
Pyrophyllite-bearing metasomatite zone in the open pit 3							
7	6114-12	Sericite quartzite	Illite	7.1	-35	2.4	+1
8	6184	Sericite-pyrophyllite quartzite	Pyrophyllite	6.4	-36	1.7	0
9	6114-9	Pyrophyllite quartzite	Pyrophyllite	6.2	-33	1.5	+3
10	6114-1	Pyrophyllite schist	Pyrophyllite	6.2	-34	1.5	+2
11	376-7	The same	The same	7.4	-30	2.7	+6
Zones of pyrophyllitization and sericite schist in the open pit 2							
12	820(1)	Sericite-pyrophyllite quartzite	Illite and pyrophyllite	7.1	-62	2.2	-24
13	820(2)	The same	The same	6.7	-57		
14	810	Sericite schist	Illite	4.3	-27	-0.6	+9
15	818	The same	The same	5.3	-43	0.6	-7
16	6174	Pyrophyllite schist	Pyrophyllite	8.6	-41	3.9	-5
Zone of paragonite-bearing mica schists in the open pit 1							
17	828	Mica-quartz metasomatite	Illite and Na mica	9.8	-55	5.1	-19
18	856	Mica schist	The same	11.1	-47	6.4	-11
19	830	The same	The same	8.3	-80	3.6	-44
20	853	The same	The same	11.4	-33	6.7	+3

Note: Isotopic composition of fluid is calculated at the temperature of 250°C.

pit 3, Fig. 2, field III) have a somewhat higher $\delta^{18}\text{O}$ than the illite schists in the southern lode (open pit 2, Fig. 2, field II). It is not ruled out that fields II and III should be merged into a common field. The micas from the latest illite-paragonite assemblage in the upper part of the northern lode are grouped into an isolated field IV in Fig. 2, which stands out by the highest $\delta^{18}\text{O}$ of 10–11‰ and elevated δD of -(30–55)‰. One analysis of this metasomatite is located out of the field IV.

In agreement with the above statements, the computation of isotopic fluid composition equilibrated with a primary mica was performed at the maximum temperature of 250°C. The temperature rise during the metamorphism should not be accompanied by a substantial diffusion of oxygen and hydrogen and a shift in isotopic compositions (Costa *et al.*, 1983). The calculation in the system quartz-water was carried out using the formula reported by Clayton *et al.* (1972) and the formulas from Cole *et al.* (1987) were applied to calcu-

tions in the system muscovite (paragonite, pyrophyllite)-water.

The inferred evolution of isotopic fluid composition at the Gai deposit is very complicated. The earliest background chlorite-illite-quartz alteration, which is absolutely predominant at the deposit, proceeded at $\delta^{18}\text{O} = 2-5\text{‰}$ and $\delta\text{D} = -(16-51)\text{‰}$ and these parameters remained during the entire time, when the deposit was formed. The fluid with such parameters occupies a transitional position between the seawater and magmatic water (Fig. 3, field I). Most likely, such fluid represents a mixture of both waters. The model permits to replace the magmatic water with metamorphic water, which resulted from the interaction of deeply circulating sea water with host volcanoclastic rocks (recycling model).

The formation of locally developed illite schists replacing the chlorite-illite-quartz metasomatites may be related to the intake of sea water into the southern

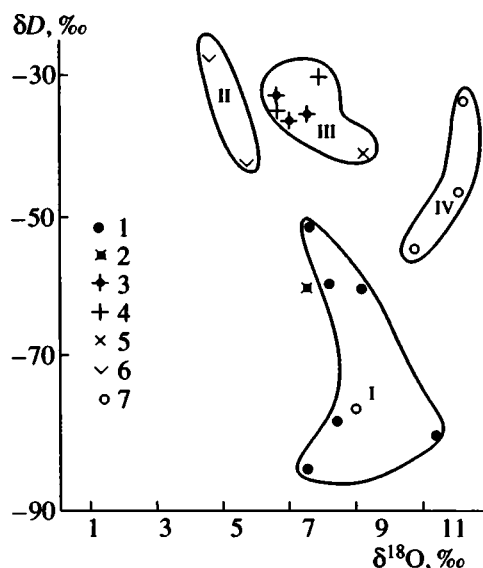


Fig. 2. Isotopic composition of micas from metasomatites at the Gai deposit. (1) Background chlorite-illite-quartz metasomatite, open pit 1 and northern profiles; (2) pyrite-illite-quartz metasomatite, open pit 2; (3) illite and pyrophyllite quartzites, open pit 3; (4) pyrophyllite schist, open pit 3; (5) pyrophyllite schist, open pit 2 (sample 6174); (6) illite schist, open pit 2; (7) illite-paragonite schist, open pit 1. Outlined fields including most analyses of rock groups: (I) background chlorite-illite-quartz metasomatite; (II) illite schist, open pit 2; (III) illite-pyrophyllite quartzite and illite-pyrophyllite schist, open pit 3; (IV) illite-paragonite schist, open pit 1.

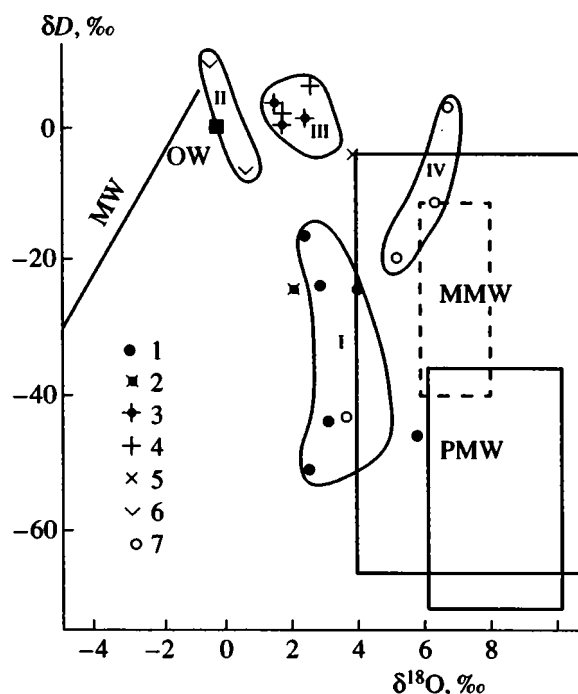


Fig. 3. Isotopic composition of water equilibrated with micas from metasomatites at the Gai deposit at 250°C. (MW) line of meteoric water; (OW) oceanic water; (MMW) metamorphic water; (PMW) primary magmatic water. The dashed box indicates the magmatic water in subduction zones (Taran *et al.*, 1989, 1997). See Fig. 2 for the legend.

part of ore-forming system (open pit 2, the least metamorphosed ore of the southern lode). Indeed, the isotopic composition of fluid strictly fits the sea water: $\delta^{18}\text{O}$ varies from +0.6 to -0.6‰ and δD —from -7 to +9‰ (Fig. 3, field II); the alteration occurred at a high water/rock ratio. The leading role of sea water is also evident for the fluid responsible for the illite-pyrophyllite-quartz alteration followed by a formation of pyrophyllite schists of the central lode (open pit 3, Fig. 3, field III). These rocks are closely related in space to the products of the above alterations. However, the process took place at a lower water/rock ratio as indicated by an increase in $\delta^{18}\text{O}$ to 1.5–1.7‰ (locally up to 2.7‰), the δD being equal to 0–6‰. The local formation of the latest illite-paragonite mica schists in the upper part of the northern lode, which replace the background chlorite-illite-quartz rocks (Fig. 3, field IV), should also be related to the impact of sea water, which was markedly enriched in the heavy oxygen isotope due to the interaction with chlorite-illite-quartz rock. The water/rock ratio is minimal, the $\delta^{18}\text{O}$ is 3.6–6.7‰, and δD varies from +3 to -19‰ (up to -44‰ in one case). These metasomatites are formed contemporaneously with recrystallization of primary ore in the central lode resulting in the deposition of secondary bornite ore at the final stage of mineral formation. The long-term

interaction of sea water with silicate rocks must shift its isotopic composition toward the metamorphic water.

The combination of isotopic and geological data provides insights into the history of the Gai deposit. The formation of the largest northern massive sulfide lode was completed by its burial beneath basaltic andesite flows and by the intense recrystallization of primary ore in the upper part of the lode, with a deposition of bornite-bearing assemblage at the expense of Cu leaching from the lower part of the lode. The formation of the enormous halo of background chlorite-illite-quartz alteration persisted to develop in the conduit and the surrounding rocks affected by deeply penetrating sea water, which interacted with silicate rocks (recycling model). An addition of magmatic water from the heat source is not ruled out.

After the burial of the northern lode, the discharge site of the hydrothermal system was displaced into its southern part, where slightly metamorphosed (not recrystallized) orebodies of the southern and partly central lodes were formed with an active participation of the sea water. The local transformation of background metasomatites into illite and pyrophyllite schists also occurred with an involvement of sea water. The further interaction of the sea water with silicate rocks gives rise to the substantial enrichment in heavy

oxygen isotope and to the formation of illite–paragonite schists in local tectonic zones of the northern lode.

The obtained empirical results and their interpretation are consistent with the data reported in literature. The deep circulation of the sea water accompanied by its interaction with heated host volcanics leads to the increase in $\delta^{18}\text{O}$ and the decrease in δD in fluid. Finally, the extensive haloes of chlorite–sericite–quartz alteration are formed within a conduit. The mixing of sea water with a magmatic fluid gives rise to the same result. A combination of several mechanisms of isotopic fluid evolution is possible at various deposits.

The increase in $\delta^{18}\text{O}$ of metasomatites with transition from massive sulfide deposits located at lower stratigraphic level to those at upper level was reported from the Noranda ore district in Canada (Hoy, 1993). This example serves as a spectacular illustration of enrichment of fluid in heavy oxygen isotope due to its interaction with silicate rocks as the fluid column ascends. Six stratigraphic levels are recognized in the Noranda district, and the sea water plays an important role in the massive sulfide ore formation at each level. The isotopic fluid parameters transitional between the sea water and magmatic (metamorphic) water were noticed for many massive sulfide deposits, in particular, for the Horn and Brunswick 12 in the Noranda district, and for deposits of the Iberian belt and the Urals (Baranov *et al.*, 1989a, 1989b; Franklin *et al.*, 1981; Lentz and Goodfellow, 1996; MacLean and Hoy, 1991; Taylor, 1967).

At the same time, both calculations and direct studies of fluid inclusions have shown that the fluids at some deposits (Mattagami in the Noranda district, Kuroko-type deposits in Japan, etc.) strictly fit the sea water in isotopic composition (Costa *et al.*, 1983; Franklin *et al.*, 1981; Taylor, 1967). This situation probably corresponds to the invasion of water directly from a marine reservoir, its mixing with a deep fluid, and the proceeding of reactions at a high water/rock ratio. Such a situation is most typical of central parts of deposits, which are close to discharge sites of conduits. The situation corresponds to conditions of the formation of quartz–chlorite and chloritoid cores at some deposits in the Noranda district. At the Uchaly and Uzel'ga massive sulfide deposits in the Urals, the sea water dominated at their periphery during the mineral formation (19 samples were analyzed). The δD of fluid in the central parts of deposits reaches 10–30‰, while at flanks, the δD value is only 0–12‰. The $\delta^{18}\text{O}$ value for the fluid at the Uchaly deposit is estimated at 1–3‰. At the Uzel'ga deposit, this parameter varies from –2 to +7‰.

Thus, the micas from various types of metasomatites at the Gai massive sulfide deposit are clearly distinct in isotopic composition. The illite from the background chlorite–illite–quartz metasomatites, which were formed and recrystallized during the entire period of mineral formation, is characterized by the least δD of (–50–85)‰ and $\delta^{18}\text{O} = 7–11$ ‰. Pyrophyllite and illite

from the pyrophyllite–quartz metasomatites and the local zones of illite and pyrophyllite schists in the southern part of the deposit have a higher δD values ($\delta D = -(25–45)$ ‰ and $\delta^{18}\text{O} = 4–9$ ‰. The latest illite–paragonite schists have transitional characteristics: $\delta D = -(30–55)$ ‰ and elevated $\delta^{18}\text{O} = 10–11$ ‰.

The proposed model of the isotopic fluid evolution at the maximum initial temperature of mica formation at 250°C assumes the circulation of deeply penetrating sea water enriched in $\delta^{18}\text{O}$ and depleted in δD due to the interaction with silicate rocks (recycling model). The mixing of sea water with magmatic or metamorphic fluids looks very attractive (Fig. 3). The formation of background alteration halo and the main volume of ore in the northern lode is related to the circulation of such transformed sea water. After the northern lode had been buried beneath the basaltic andesite flow, the discharge area of geothermal system was shifted southward where the repeated invasions of sea water gave rise to the formation of pyrophyllite–quartz metasomatites, the slightly metamorphosed orebodies of the southern lode, and the subsequent pyrophyllite and illite schists within shear zones. The further interaction of this water with silicate rocks and the respective increase in $\delta^{18}\text{O}$ was completed by a formation of illite–paragonite schists.

At that time, the buried northern lode underwent an intense recrystallization with a formation of bornite assemblage. In general, the substantial role of sea water in the formation of metasomatic haloes of ore deposits hardly casts any doubt.

ACKNOWLEDGMENTS

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A New Type of Open Fracturing in the Rocks

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Abstract—The finest open fractures (ultramicrofractures) were found from the study of surface density of open fractures in the rocks from the super-deep Uralian borehole SG-4. The high-resolution method of the registration of open fractures in the rocks is described. The typical structures of systems formed by open fractures are shown and their genesis is proposed.

A new type of fracturing was found from the study of physical properties of the rocks, which were taken from the super-deep Uralian borehole SG-4 located in the Sverdlovsk district, 4 km southwest of Verkhnyaya Tura.

We studied the core from 5350-m borehole, which recovered the Lower–Upper Silurian Immenovka and Kaban (the upper part) formations. The core is represented by predominant volcanoclastic rocks, as well as volcanic, volcanosedimentary, and subordinate plutonic rocks (Andreeva *et al.*, 1982). They are highly altered by prehnitization, epidotization, chloritization, silicification, sericitization, hematization, and other processes. In separate interbeds, the rocks are replaced by metasomatites. The lowermost part of the section contains the interbeds of siliceous siltstones, silty mudstones, and carbonaceous–siliceous rocks.

In order to measure the gas permeability and surface density of the open fractures along the three directions,

the cubes of $4 \times 4 \times 4$ cm in size were cut from the core samples. The “end pieces” of core cuttings were used for measurement of open porosity by means of liquid saturation (State standard GOST 26450.1-85). To increase the measurement accuracy, the transformer oil was used as a saturating liquid (Potapov, 1990). The applied technique make it possible to measure an open porosity of low-capacity rocks with relative error less than 10%.

The study of the capacity characteristics showed that the rocks recovered by the Uralian borehole SG-4 have a fairly low porosity (Table 1). The primary pores are almost completely filled with secondary minerals. Relics of primary pores are isolated and mainly confined to volcanic amygdules and fragments of the volcanoclastic rocks. In spite of a fairly low open porosity, the studied rocks have considerable permeability (Table 2).

The above relationship of gas permeability and open porosity may be observed if the cavity space in the

Table 1. Open porosity of the rocks from the Uralian borehole SG-4

Rock types	Occurrence frequency (%) of samples with open porosity (%)					Average, %	Number of samples
	0–0.4	0.4–0.8	0.8–1.2	1.2–1.6	1.6–1.8		
Volcanic	53.6	37.5	4.8	1.3	2.8	0.45	183
Volcanoclastic	31.7	44.6	20.1	2.8	0.8	0.59	494
Volcanosedimentary	43.8	44.0	12.2	–	–	0.47	109
Plutonic	37.7	53.2	9.1	–	–	0.49	42

Table 2. Filtration properties of rocks from the Uralian borehole SG-4

Rocks	Gas permeability, fm ²			Number of samples
	minimal	maximal	geometric mean	
Plutonic	0.000042	0.0739	0.000215	19
Volcanic	0.0000301	0.061	0.000122	52
Volcanoclastic	0.000022	2.47	0.00615	74
Volcanosedimentary	0.0000085	0.305	0.00016	25

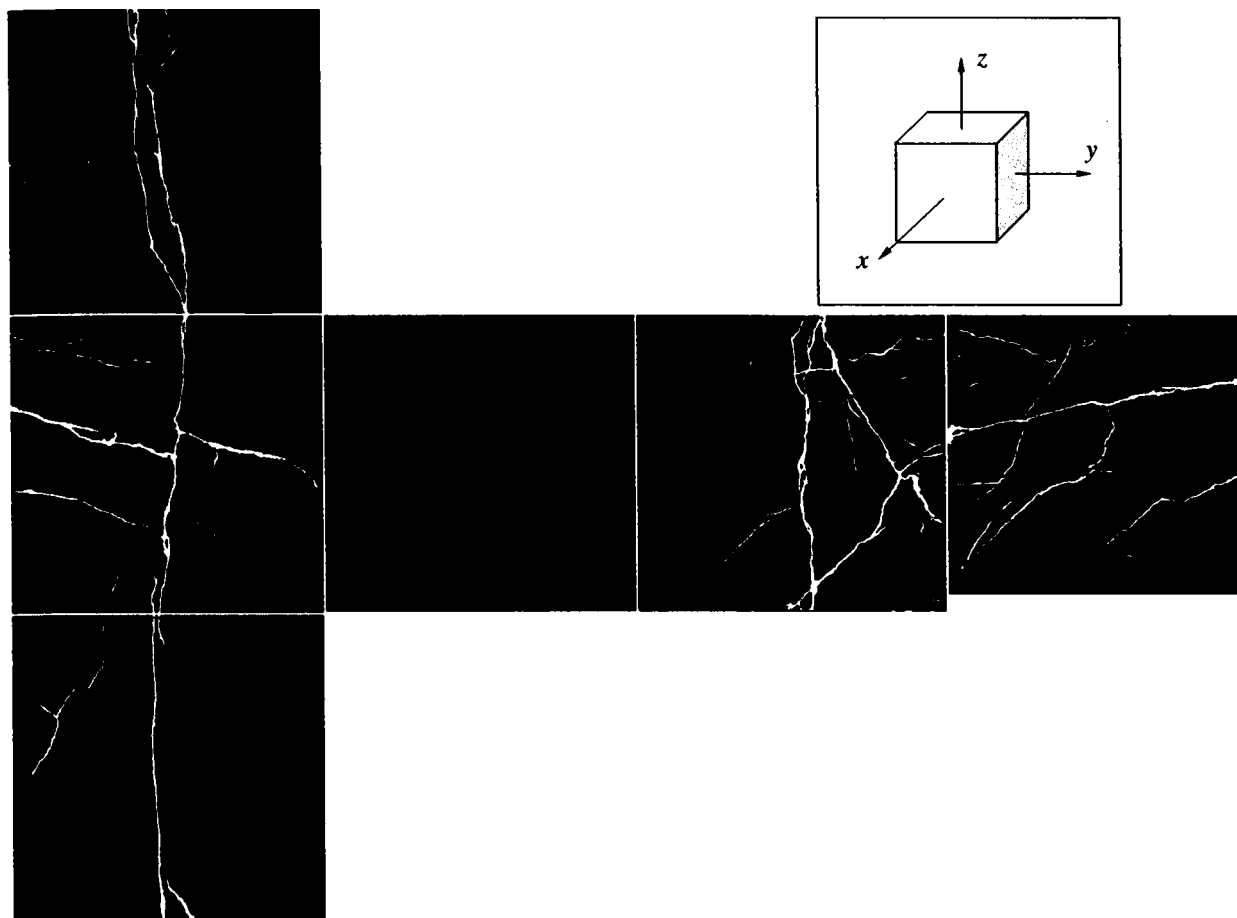


Fig. 1. Sample 28774, depth 4375.04 m. Tuffite of mixed composition containing two intersecting systems of tectonic fractures with subsidiary sinuous fractures thinning out different directions.

$K_{op} = 0.38\%$; $(K_{gp})_x = 2.47 \text{ fm}^2$, $(K_{gp})_y = 2.21 \times 10^{-4} \text{ fm}^2$, $(K_{gp})_z = 5.93 \times 10^{-1} \text{ fm}^2$, where K_{op} is an open porosity, %; K_{gp} denotes a gas permeability coefficient, z is direction subparallel to core axis; x , y are orthogonal directions in planes almost normal to core axis.

rocks was formed by open fractures. To study the structure of the fracture-induced cavity space of the rocks, the surface density of open fractures was measured with the following high-resolution method (*Sposob...*, 1994). Cubic specimens were saturated with 1N sodium sulfide. The excess solution at the surface was removed with distilled water. Then, photographic film pieces were attached to specimen faces in a special apparatus under the pressure of 5 MPa for 30 min.

Under the action of confining compression, some part of solution from the cavity space was squeezed out on the surface and contacted with films. As a result, sodium sulfide reacted with silver chloride of emulsion layer and formed the dark-colored silver sulfide above the fracture channels. After the termination of reaction, the pressure in the apparatus was decreased to an atmospheric one. Then, the specimens were taken from the apparatus, and the films from faces were removed and

Table 3. Surface density of the open fractures in the samples from the Uralian borehole SG-4

Rocks	Surface density of open fractures, m^{-1}			Number of samples
	minimal	maximal	average	
Plutonic	22	181	65	6
Volcanic	0	153	43	11
Volcaniclastic	0.14	364	114	30
Volcanosedimentary	0	47	27	8

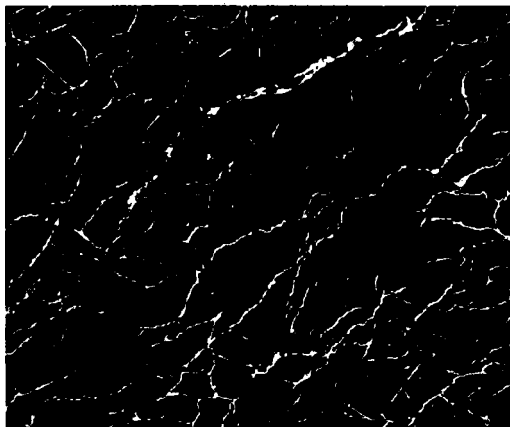


Fig. 2. Sample 23642, interval 3820–3826 m. Ultramicrofractured tuff gritstone. The fracture thickness is less than 0.001 mm. Magn. 3.

$$K_{op} = 0.7\%; K_{gp} = 8.5 \times 10^{-3} \text{ fm}^2.$$

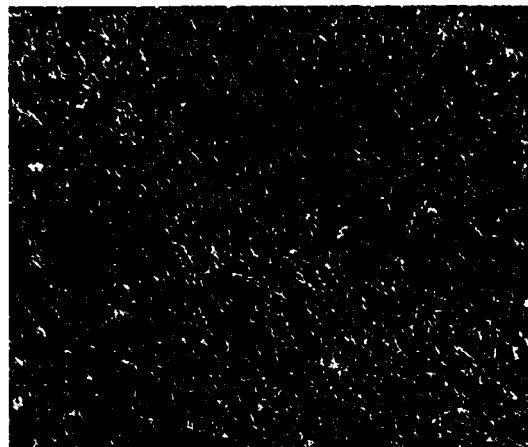


Fig. 3. Sample 18946, interval 3101–3108 m. Sandy tephroid with ultramicrofractures. The fractures surround or occasionally cut the fragments. The fracture width is less than 0.001 mm. Magn. 3.

$$K_{op} = 1.0\%; K_{gp} = 5.6 \times 10^{-4} \text{ fm}^2.$$



Fig. 4. Sample 29559, interval 4507.6–4515.7 m. Sandy tuffs with two systems of tectonic fractures. Some blocks contain ultramicrofractures. Magn. 3.

$$K_{op} = 0.66\%; K_{gp} = 2.26 \text{ fm}^2.$$



Fig. 5. Sample 22330, interval 3669.7–3765.0 m. Porphyritic basalt with subhorizontal open fissures. The pyroxene fragments are crosscut by ultramicrofractures. Magn. 3.

$$K_{op} = 0.46\%; K_{gp} = 4.3 \times 10^{-2} \text{ fm}^2.$$

treated in fixing agent to eliminate the excess silver chloride from emulsion layer. The silver sulfide remained in the emulsion layer and traced the fracture channels. The photo prints, which were made up after the washing and drying of the films, were used to deter-

mine the surface density of open fractures with the known methods (Padushinskii, 1970; Saltykov, 1976).

The obtained data indicate a great diversity of types and genesis of open fractures in the rocks from the Ura-

Table 4. The gas permeability and distribution of predominant type of open fractures in the rocks from the Uralian borehole SG-4

Types of open fractures in rock samples	Occurrence frequency (%) of samples with permeability (fm ²)					Average, fm ²	Number of samples
	$1 \times 10^{-5} - 1 \times 10^{-4}$	$1 \times 10^{-4} - 1 \times 10^{-3}$	$1 \times 10^{-3} - 1 \times 10^{-2}$	$1 \times 10^{-2} - 1 \times 10^{-1}$	$1 \times 10^{-1} - 1.0$		
Microfractures	25.5	25.5	23.0	11.5	14.5	0.0014	35
Ultramicrofractures	27.0	37.0	24.0	9.5	2.5	0.0006	41

lian superdeep borehole. The tectonic fractures are the most widespread in the studied rocks (Fig. 1).

The fractures are linear or slightly sinuous with comparatively smooth walls. They are characterized by different thicknesses and spatial orientations. The rocks contain from one to several fracture systems intersecting at right or acute angles. The permeability in the rocks crossed by fractures depends on the direction of gas filtration. The permeability along the core axis is usually higher than that along the normal direction. This suggests that the recovered section of the Uralian borehole SG-4 does not contain the fluid-confining rocks. The surface density of open fractures ranges from 0 to 364 m⁻¹. The volcanoclastic rocks are characterized by increased open fracturing (Table 3).

In addition to tectonic fractures, the studied samples contain net-like open fractures surrounding or occasionally cutting the fragments of volcanoclastic rocks (Figs. 2, 3). The net-like fractures are significantly less than one micron wide and may be assigned to ultramicrofractures. It should be noted that the permeability of rocks with mainly ultramicrofracture-produced cavity space is very low (Table 4).

As distinctly seen in Figs. 2 and 3, the cavity space formed by ultramicrofractures demonstrate some ordering. We may suggest that the ultramicrofractures were originated under the action of confining compression and high temperature of the regularly distributed quasi-continuous fracture with continuous self-healing (Rozanov, 1965). The sharp decrease of confining compression terminates the plastic flow, thus producing the rock discontinuity and pressure-release fractures (Pavlova, 1975).

Such a mechanism of the formation of net-like ultramicrofractures may be partially confirmed by results of the study of surface density of open fractures in tuff specimen taken from a depth of 4507.6–4515.7 m (Fig. 4). The cavity space of the specimen predominantly consists of tectonic fractures of two generations, while ultramicrofractures are mainly confined to a plastically deformed block that experienced high confining compression.

Judging from the shape of open fractures and their relations with fragments and minerals, some open fractures may be related to lithological processes or sharp temperature decrease on the cooling of lava flows (Fig. 5). The specimens also may contain technogenic fractures (Fig. 6).

The contribution of technogenic factors to the formation of cavity space in the plutonic rocks may be confirmed by relatively high porosity (Table 1). We may suggest that these rocks partially preserved a primary porosity owing to the presence of volcanic gas bubbles trapped during the melt solidification. The pores are less than one micron in size. The microfractures are formed under the pressure of volcanic gas during the core uplift from the borehole bottom. This process pro-

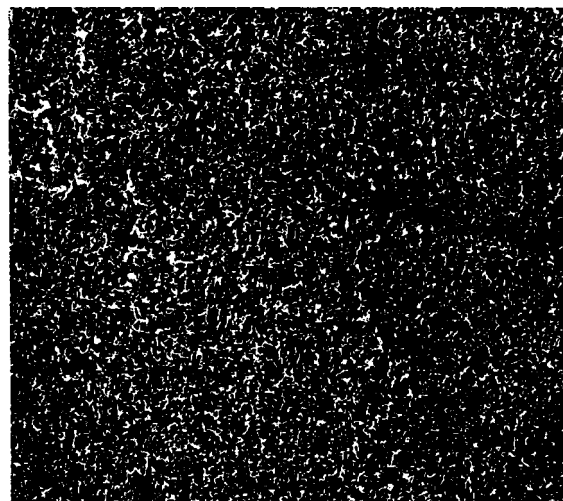


Fig. 6. Sample 20862, interval 3456.4–3461.9 m. Diorite with numerous thinning out microfractures. The width is < 0.001 mm. Magn. 6.

$$K_{op} = 0.91\%; K_{gp} = 7.7 \times 10^{-3} \text{ fm}^2.$$

duces an intricate cavity space, which is well seen in the photo prints of traces of open fractures (Fig. 6).

The application of a new method of surface density measurement of open fractures in the rocks of the Uralian borehole SG-4 revealed a new type of fracturing, whose detailed study will refine the existing concept of the formation of fold systems.

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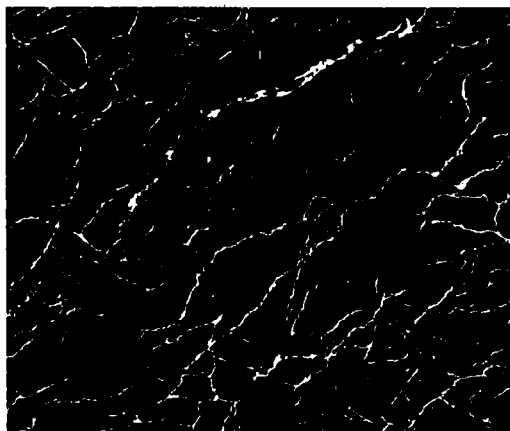


Fig. 2. Sample 23642, interval 3820–3826 m. Ultramicrofractured tuff gritstone. The fracture thickness is less than 0.001 mm. Magn. 3.

$$K_{op} = 0.7\%; K_{gp} = 8.5 \times 10^{-3} \text{ fm}^2.$$

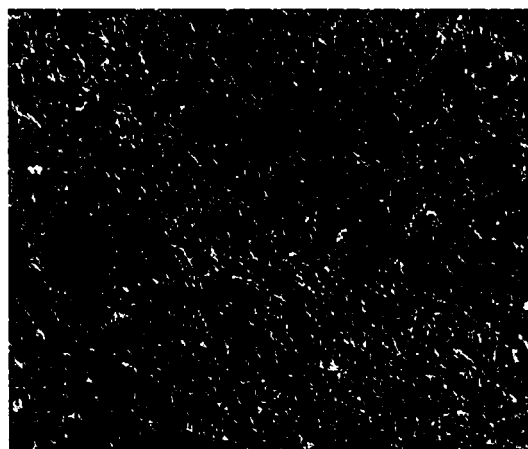


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$$K_{op} = 1.0\%; K_{gp} = 5.6 \times 10^{-4} \text{ fm}^2.$$

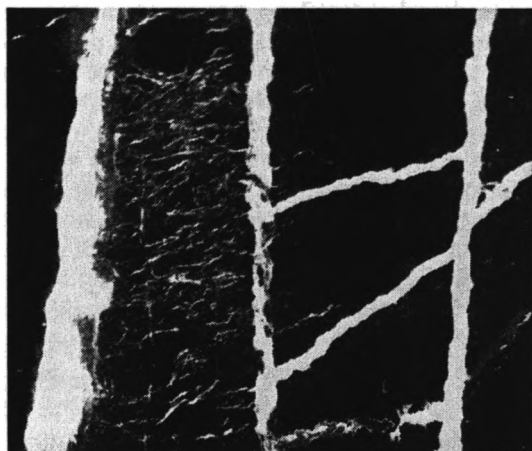


Fig. 4. Sample 29559, interval 4507.6–4515.7 m. Sandy tuffs with two systems of tectonic fractures. Some blocks contain ultramicrofractures. Magn. 3.

$$K_{op} = 0.66\%; K_{gp} = 2.26 \text{ fm}^2.$$



Fig. 5. Sample 22330, interval 3669.7–3765.0 m. Porphyritic basalt with subhorizontal open fissures. The pyroxene fragments are crosscut by ultramicrofractures. Magn. 3.

$$K_{op} = 0.46\%; K_{gp} = 4.3 \times 10^{-2} \text{ fm}^2.$$

treated in fixing agent to eliminate the excess silver chloride from emulsion layer. The silver sulfide remained in the emulsion layer and traced the fracture channels. The photo prints, which were made up after the washing and drying of the films, were used to deter-

mine the surface density of open fractures with the known methods (Padushinskii, 1970; Saltykov, 1976).

The obtained data indicate a great diversity of types and genesis of open fractures in the rocks from the Ura-

Table 4. The gas permeability and distribution of predominant type of open fractures in the rocks from the Uralian borehole SG-4

Types of open fractures in rock samples	Occurrence frequency (%) of samples with permeability (fm ²)					Average, fm ²	Number of samples
	$1 \times 10^{-5} - 1 \times 10^{-4}$	$1 \times 10^{-4} - 1 \times 10^{-3}$	$1 \times 10^{-3} - 1 \times 10^{-2}$	$1 \times 10^{-2} - 1 \times 10^{-1}$	$1 \times 10^{-1} - 1.0$		
Microfractures	25.5	25.5	23.0	11.5	14.5	0.0014	35
Ultramicrofractures	27.0	37.0	24.0	9.5	2.5	0.0006	41

lian superdeep borehole. The tectonic fractures are the most widespread in the studied rocks (Fig. 1).

The fractures are linear or slightly sinuous with comparatively smooth walls. They are characterized by different thicknesses and spatial orientations. The rocks contain from one to several fracture systems intersecting at right or acute angles. The permeability in the rocks crossed by fractures depends on the direction of gas filtration. The permeability along the core axis is usually higher than that along the normal direction. This suggests that the recovered section of the Uralian borehole SG-4 does not contain the fluid-confining rocks. The surface density of open fractures ranges from 0 to 364 m⁻¹. The volcanoclastic rocks are characterized by increased open fracturing (Table 3).

In addition to tectonic fractures, the studied samples contain net-like open fractures surrounding or occasionally cutting the fragments of volcanoclastic rocks (Figs. 2, 3). The net-like fractures are significantly less than one micron wide and may be assigned to ultramicrofractures. It should be noted that the permeability of rocks with mainly ultramicrofracture-produced cavity space is very low (Table 4).

As distinctly seen in Figs. 2 and 3, the cavity space formed by ultramicrofractures demonstrate some ordering. We may suggest that the ultramicrofractures were originated under the action of confining compression and high temperature of the regularly distributed quasi-continuous fracture with continuous self-healing (Rozanov, 1965). The sharp decrease of confining compression terminates the plastic flow, thus producing the rock discontinuity and pressure-release fractures (Pavlova, 1975).

Such a mechanism of the formation of net-like ultramicrofractures may be partially confirmed by results of the study of surface density of open fractures in tuff specimen taken from a depth of 4507.6–4515.7 m (Fig. 4). The cavity space of the specimen predominantly consists of tectonic fractures of two generations, while ultramicrofractures are mainly confined to a plastically deformed block that experienced high confining compression.

Judging from the shape of open fractures and their relations with fragments and minerals, some open fractures may be related to lithological processes or sharp temperature decrease on the cooling of lava flows (Fig. 5). The specimens also may contain technogenic fractures (Fig. 6).

The contribution of technogenic factors to the formation of cavity space in the plutonic rocks may be confirmed by relatively high porosity (Table 1). We may suggest that these rocks partially preserved a primary porosity owing to the presence of volcanic gas bubbles trapped during the melt solidification. The pores are less than one micron in size. The microfractures are formed under the pressure of volcanic gas during the core uplift from the borehole bottom. This process pro-

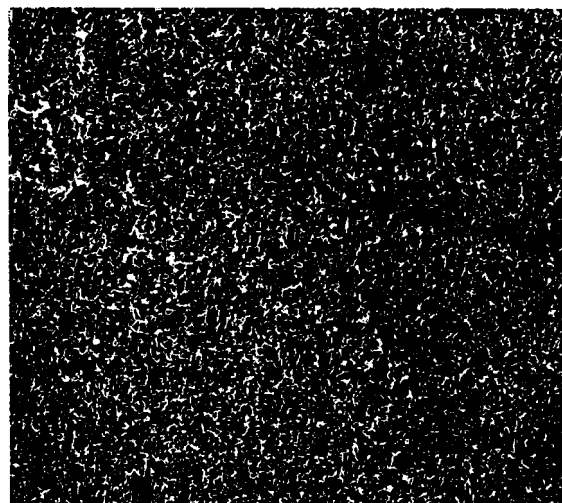


Fig. 6. Sample 20862, interval 3456.4–3461.9 m. Diorite with numerous thinning out microfractures. The width is < 0.001 mm. Magn. 6.

$K_{op} = 0.91\%$; $K_{gp} = 7.7 \times 10^{-3} \text{ fm}^2$.

duces an intricate cavity space, which is well seen in the photo prints of traces of open fractures (Fig. 6).

The application of a new method of surface density measurement of open fractures in the rocks of the Uralian borehole SG-4 revealed a new type of fracturing, whose detailed study will refine the existing concept of the formation of fold systems.

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CRITICS

A New Genetic Model of Phosphorite Formation (Critical Analysis of Publications by V.N. Kholodov and R.K. Paul)

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The problem of the formation of commercial (granular and microgranular) phosphorites is intensely discussed. A spectrum of proposed mechanisms range from direct chemical precipitation to the extraction of P from organic remains, and different forms of biogenic factor. During the last 30–40 years, the problem was discussed very thoroughly, and only large-scale examinations, new observations, and experiments could provide reliable solutions. Nevertheless, V.N. Kholodov and R.K. Paul have suggested a new model of the phosphorite formation (Kholodov, 1997; Kholodov and Paul, 1993, 1995a, 1995b, 1996a, 1996b).

This communication presents a critical review of absolutely new ideas reflected in the series of publications mentioned above.

The main hypothesis is based on hydrochemistry of the modern Black Sea and materials from the Karatau phosphorite-bearing basin. It is emphasized that the H₂S-contaminated water of the Black Sea is enriched in Si and P. It is understandable that stagnant conditions are favorable for the decomposition of dead organisms and the accumulation of these elements. During the long history of the Black Sea, such a situation, however, never resulted in the formation of any phosphorite accumulations in the coastal, shelf, or deeper zones of the basin. This fact does not embarrass authors of the model. They consider the deep-water part of the Early Cambrian Karatau Basin, which is located in low latitudes, as an analogue of the Black Sea with anoxic conditions, whereas the shallow-water carbonate platform is compared to the shelf with intense carbonate accumulation. In their opinion, deep waters of the H₂S-contaminated zone moving toward shoals during transgressive phases of the basin development lose H₂S but preserve Si and P. In the coastal zone, they replace soft parts of bacterial–algal mats with phosphorus. Owing to such reaction with “strong phosphoric acid,” phosphatized and lithified parts of mats are disintegrated. Subsequently, fragments of these mats are transformed into phosphate grains and accumulated as phosphorite layers. Similarly, silica replaced carbonates of biogenic buildups. However, silica fragments were not formed for some reason.

The proposed model includes the following two principal postulates: (1) penetration of deep waters of the H₂S-contaminated zone to the littoral zone and (2) their phosphate-forming influence on mats. However, there are no examples of such phosphatization (as well as silicification) in modern conditions. Although, there are examples of deep H₂S-bearing waters approaching coasts, which are not considered by authors.

The upper boundary of H₂S-contaminated waters in the Black Sea was only recently at the depth of about 200 m. At present, it is located at the depth of several dozens of meters. The Black Sea transgression is continuing over hundreds of millennia (e.g., ria-type coasts, ingression in depressions of the coastal land, and others). During the recent decades, H₂S-contaminated waters approach the coast (for instance, near Odessa) several times in a single season. This occurs under winds blowing from or along the shore. They drive away warm surface waters, which results in the upwelling of deep cold (+16 to +19°C), relatively H₂S-rich water. This phenomenon is evident from odor, opalescence, and fauna death. These are the waters discussed in considered publications. The coastal zone hosts Pontian limestones and also rock breakwaters constructed several dozens of years ago 30 m away from the shore. They are covered by algal and other biogenic films, which have contact with deep waters, but no signs of phosphatization and silicification are observed. It is well known, however, that organic matter is almost instantly phosphatized. In addition, solely carbonates were frequently accumulated along the southern periphery of the Black Sea basin in the Pontian time.

Thus, only assumptions based on specific observations in the Karatau Basin remain. Kholodov and Paul should have substantiated the fact of the existence of the H₂S-contaminated water zone in this paleobasin. The presence of black shale facies cannot automatically indicate that the water column above such sediments was saturated with hydrogen sulfide. Kholodov (1992) himself noted that “... the presence of radiolarians, less commonly sponge spicules (Ankinovich, 1961), probable remains of diatom valves (Ergaliev and Azerbaev, 1986; Gapeev, 1995), along with the complete absence

of remains of benthic communities, in these rocks indicate anoxic conditions....” But sponges are typical benthic organisms and could not survive at the bottom of the anoxic basin. Their presence excludes any suspicions with regard to bottom anoxic conditions. In addition, black shales of the Karatau phosphorite-bearing formation enclose abundant ichnofossils, fucoids, as well as phosphorite and spongolite interbeds, i.e., aerobic sediments. It is evident that, in the considered case, anoxic conditions can appear only within mud.

The correlation of the Kurumsak Formation (Ankinovich, 1961) referred to the Middle Cambrian with the Lower Cambrian Chulaktau Formation of Lesser Karatau is very unreliable. There are observations suggesting that the Chulaktau Formation wedges out toward the Kurumsak Formation along the entire southwest stretch of Lesser Karatau, which is logical, because the latter is younger and its accumulation was a result of further sea transgression. Greater and Lesser Karatau are separated by the regional strike-slip fault. Substantial facies differences developed in these regions do not allow their stratigraphic units to be united into a common “rock” basin.

It should be noted that all rocks of the phosphorite-bearing formation are black in the nonoxidized state and contain noticeable amounts of C_{org} and pyrite, i.e., they also can be referred to “anoxic” facies, but, following Kholodov and Paul, they were formed owing to the phosphatization of biogenic substances by former H_2S -contaminated waters already in the oxidizing environment.

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However, some essential properties of phosphate grains are not analyzed in the proposed model simply because they do not conform to the model. For instance, most grains from Karatau are represented by oncolites, which previously were not separated from true oolites. The core of oncolite is represented by phosphate fragment, which is successively enveloped by cyanobacterial films that are subsequently also phosphatized. Thus, oncolites represent products of two phosphatization stages, which occur, though, in different environments. The first stage corresponds to the formation of phosphate cores composed, as is established now, of microbial nonlaminated mats, sometimes with sponge

remains. The mats include varieties formed in the supratidal zone and even in closed lagoons, whose analogues are known from modern arid coasts. How could their phosphatization occur in the framework of the proposed model, if there is no connection with the sea? Oncolite shells, in turn, reflect settings of core (grain) rounding. This process allows the micromat to overgrow the shells. As soon as such particles stop moving, their phosphatization commences, i.e., only then, the replacement of mat envelopes by phosphate can occur. Inasmuch as the arrangement of enveloped grains usually is sufficiently compact (frequently they even form clusters), the upper part of the shell could be phosphatized in line with the proposed model, but this process is absolutely excluded for its inner layers. Nonetheless, oncolites have either all layers phosphatized or none; for a vague reason, they never turn into grains.

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CRITICS

Strange Inaccuracies (A Reply to Critical Comments by E.L. Shkol'nik *et al.*, “A New Genetic Model of Phosphorite Formation”)

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Beginning from the 1990s, we published 12 articles in different periodicals dedicated to the problem of phosphorite formation. Authors of critical comments published in this issue consider arbitrarily six articles published in different years. In line with their own understanding of the problem, they arrange the articles as representing a genetic model and further consider some of its separate ideas and the model as a whole.

It is stated from the very beginning that the hypothesis is based on hydrochemistry of the modern Black Sea. This is not true. We analyzed materials, which characterize the phosphorus behavior in waters of many modern seas and oceans as well as in interstitial waters of different modern basins. As a result, it was established (Kholodov and Paul, 1993, table; 1996, Table 1) that the manifold enrichment of interstitial waters with phosphorus is related to sulfate-reduction processes and microbiological decomposition of organic matter at the stage of sediment diagenesis. Later, using the Black Sea as an example, it was shown that phosphorus is accumulated in H_2S -contaminated waters at the expense of both decomposition of planktonogenic organic matter and “processing” of phosphate suspension accumulated in mud (Kholodov and Paul, 1995). Furthermore, the cited article discusses not “phosphorite accumulation,” as is stated by our opponents, but “phosphate accumulation” in waters of the H_2S -contaminated zone (see list of references), which, as is well known, is not the same.

We considered the Black Sea as a model allowing the geochemical behavior of phosphate suspension to be understood and sources of accumulation of P_2O_5 dissolved in H_2S -contaminated waters to be defined.

The further analysis (Kholodov, 1997; Kholodov and Paul, 1999) of published data led us to the following conclusion: waters of all modern basins with H_2S -contaminated waters are enriched, in different proportions, by dissolved P, Si, Mn, and Fe; the H_2S -contaminated zones are easily destroyed by oxygen-rich waters; and geochemical barriers that appear during this process often promote the precipitation of ore components. It is conceivable that this mechanism was responsible for the formation of phosphate–ferroman-

ganese mineral association in Recent sediments of the Gotland Basin of the Baltic Sea (Emel'yanov, 1981; Blazhchishin and Lukashev, 1981), in carbonate sediments of Mount Aves, Cariaco Basin (Marlowe, 1971), on the shelf of the Karkinitiskii Bay of the Black Sea (Mitropol'skii *et al.*, 1982), and in some other regions of the world. It is easy to see that we estimated the role of H_2S – CO_2 systems in the modern sedimentary phosphate hydrochemistry based not only on materials from the Black Sea.

Furthermore, the absence of Recent phosphorites in sediments of this basin is easily explained from the point of view of the increase or stability of the H_2S -contaminated zone; only the destruction of hydrogen sulfide accumulations and the oxidation of H_2S to SO_4^{2-} by oxygen promotes the development of processes of mineral and ore formation.

Turning further to the structure of Tommotian sequences of Greater and Lesser Karatau, our opponents argue that, in this case, H_2S contamination of the water column is not substantiated; they completely and, without any analysis, ignore conclusions of outstanding specialists such as N.G. Kassin, N.M. Salov, S.G. Ankinovich, and others, who postulated the presence of H_2S in bottom waters of the Karatau V-bearing basins, as well as the existence of the geochemical markers such as the stagnation coefficient or Mo/Mn ratio in sediments.

It should be remembered that molybdenite (MoS_2) possesses the maximum energy of the crystalline lattice as compared with pyrite, sphalerite, galena, cinnabar, and other sulfides (Saukov, 1951). Therefore, in case that Mo, Fe, Zn, Pb, and Hg simultaneously enter the H_2S -contaminated water, Mo will first form sulfide and enrich bottom sediments in the form of the solid phase. On the contrary, Mn will intensely be dissolved under conditions of H_2S contamination of water, and its concentration in sediments will be reduced.

In basins with the oxic regime and well-aerated waters, the situation will be quite opposite: Mo will be dissolved in water, whereas Mn will be accumulated in sediments.

Stagnation coefficient (Mo/Mn) values in rhythmically bedded phthanites and shales from the Tommotian sequences of Karatau (Kazakhstan)

Area, deposit, formation	Content, %		Mo/Mn
	Mo	Mn	
Northwestern Karatau, Bala-sauskandyk, Kurumsak Formation	0.0009	0.01	0.09
	0.0111	0.02	0.55
	0.0055	0.01	0.55
	0.003	0.02	0.15
	0.0057	0.008	0.71
	0.0045	0.02	0.22
Talas Alatau, Dzhebagly, Kurumsak Formation	0.0002	0.01	0.02
	0.0015	n.d.*	—
	0.001	0.02	0.05
	0.0016	0.01	0.16
	0.0013	0.04	0.03
Lesser Karatau, Koksuy River, Chulakta Formation	0.0011	0.05	0.022
	0.0016	0.038	0.042

* (n.d.)—not detected.

The subaqueous reducing diagenesis does not change evidently but preserves initial relations between Mo and Mn in seawater. Therefore, the Mo/Mn ratio in rocks represents a peculiar indicator of the gas regime in bottom waters. The study of Tertiary sequences of the Ciscaucasia region, based on ecological investigations by N.A. Andrusov, A.D. Arkhangel'skii, B.P. Zhizhchenko, E.V. Liverovskaya, and N.M. Strakhov, showed that the stagnation coefficient is estimated to be 0.0n, in the H₂S-contaminated basins and 0.00n in oxic basins (Kholodov and Nedumov, 1991).

The table in this work shows stagnation coefficient values characteristic of the Tommotian rhythmically bedded sequences of Karatau; it is evident that Kurumsak phthanite-shaly rocks of Greater Karatau and phthanite-shaly rocks of the middle part the phosphorite-bearing Chulakta Formation of Lesser Karatau were formed in H₂S-contaminated basins.

Arguments of our opponents that sponge spicules recorded in siliceous sequences of Greater Karatau indicate that the oxic regime of bottom waters should hardly be taken into consideration, because these allochthonous remains can easily be transported by waves and currents and buried far from source sponge reefs and thickets.

As for ichnofossils and fucoids, according to Eganov and Sovetov (1979), they are developed in the areas where thin laminae of pelletal phosphorites intercalate with laminae of clayey and siliceous shales, i.e., in the facies representing the transition between two settings. We state that, within the sequence of persistently developed phthanites, fucoids are commonly missing.

It should be emphasized that, in the most complete sections of the phosphorite-bearing Chulakta Formation of Lesser Karatau, the gradual transition from sediments formed in aerobic sea environments to sediments accumulated under the influence of allochthonous H₂S-contaminated waters and, finally, to those deposited in the zone of the stable H₂S-contamination distinctly coincides with the biostratigraphic zonality established by Missarzhevskii and Mambetov (1981): the distribution of conodonts, phytolites, hyolithelminths, sclerites, anabarids, chancellorians, tammotiids, and other species usually coincides with that of aerobic facies.

The correlation between the Kurumsak sequences of Greater Karatau and Talas Alatau as well as between sequences of the Chulakta phosphorite-bearing formation of Lesser Karatau represents a particular problem; it was considered in works by V.N. Kholodov, B.M. Keller, N.M. Chumakov, G.Kh. Ergaliev, and some other researchers. The absolute geochronology of the Kumysta granitoid massif, the stratigraphic zonality of Vendian-Cambrian sequences of Lesser Karatau substantiated in the book by Missarzhevskii and Mambetov (1981), and the finds of Vendian-Cambrian acritarchs in the Kuraila and Baikonur formations of Greater Karatau (Kras'kov and Smirnova, 1982) allow the Baikonur and Berkut formations from these different regions to be correlated.

On the other hand, the zonality of carbonate facies of the Tamda Formation established by Ergaliev and Azerbaev (1986), based on trilobites, represents a reliable basis for the correlation of the Kokbulak Formation of Greater Karatau with the Amgian and Aksaian stages of the Middle-Upper Cambrian and the correlation of the Tamda Formation of Lesser Karatau with the Atdabanian and Aksaian stages of Lower-Upper Cambrian.

If it is true, the Kurumsak V-bearing phthanite sequence of Greater Karatau can be correlated, with sufficient confidence, with the phosphorite-bearing Chulakta Formation of Lesser Karatau. This is supported by the development of siliceous-phosphorite beds corresponding to coastal areas of the Mynzhilka anticline in the central areas of Greater Karatau as well as by the distribution of V-bearing phthanites in the most complete sections of the phosphorite-bearing basin. In other words, the Tommotian portion is sufficiently well correlated in different sections of the considered region.

In the 1990s, when we began the systematic study of phosphate pellets from the Karatau region, ideas about the mechanism of their formation were extremely variable. Sokolov (1991) believed that they are of the chemogenic origin, Eganov (1988) thought that they represent typical intraclasts, whereas Smirnov (1972) viewed them as representing micronodules.

The study of phosphate pellets using two autonomous methods, namely the electron microscopic

method (Rozanov and Zhegallo, 1989) and the morphometric method, i.e., the study of forms and dimensions of phosphate particles in different settings (Kholodov and Paul, 1995) allowed us to consider them as bacterial-algal microcolonies. In this connection, appeals of our opponents to reject the morphometric method and, in turn, to prefer the scanning electron microscopy become abstruse. We think that the system method will always be more preferable in lithology in comparison with any biased investigation methods of complex objects.

Finally, the critical review by E.L. Shkol'nik *et al.* contains many inaccuracies. It is untrue that an absolutely new model of phosphorite formation, previously never suggested, is considered. In our works, we developed concepts of N.G. Kassina, N.M. Salov, S.G. Ankinovich, and E.A. Ankinovich.

It is unlikely that deep waters can lose hydrogen sulfide on the shelf simultaneously preserving silicon and phosphorus. It is impossible to agree that the transgression of the Black Sea continues for hundreds of years. Further, it is doubtful that, as soon as biogenic particles stop moving, their phosphatization should start. It is also unclear to determine why the appearance of toxic H_2S -contaminated waters in the shallow water zones should result in the intense plankton blooming.

It seems that our opponents are not very anxious to search for the scientific truth!

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CHRONICLE

The Third Ural Regional Lithological Meeting

The Third Ural Regional Lithological Meeting was held in Ekaterinburg on September 16–17, 1998 by the Interdepartmental Lithological Committee of the Russian Academy of Sciences (RAS) at the Ural State Mining and Geological Academy (UGGGA). It was devoted to the fundamental geological problem of regularities in the structure of sedimentary sequences. Most attention was devoted to the sedimentogenesis and lithogenesis, i.e., general problems of the sedimentary process and compositional evolution under different paleogeographic environments. The problem of the formation and location of some types of mineral deposits were discussed as well.

More than 40 scientific and production institutions from Moscow, St. Petersburg, the Urals, Novosibirsk and other regions took part in the meeting. Four sessions were held for two days and only 13 were presented among 36 declared papers because of the absence of the authors (for the lack of transportation funds). The reports were dedicated to general problems of sedimentary geology (sedimentogenesis and lithogenesis), sedimentary deposits in general, and some regions of the Urals and adjacent areas.

The facies analysis was discussed in the following papers:

Sedimentogenesis of Modern Areas of the Coastal Peat Formation (P.P. Timofeev)

Lithogenesis and Two Types of the Early Metamorphic Alterations of Sedimentary Complexes (O.V. Yapa-skurt)

The Sedimentologic Structure and Depositional Environments of the Vendian Molasse, the Yenisei Range (Yu.K. Sovetov and V.V. Blagovidov).

The lithologic regional problems were elucidated in reports:

A General Theory of the Cyclic Analysis and Problems of Mesocycles (V.G. Frolov)

Paleozoic Carbonate Platforms in the History of the Urals and Adjacent Regions (B.I. Chuvashov and V.P. Shuiskii)

Facies Associations in Riphean Sections of the Volga-Urals Region (A.V. Maslov and M.V. Isherskaya)

Lithofacies Complexes of Valleys and Related Depositional Conditions (V.I. Kopnin and V.V. Oborin)

Peculiarities of Formation of the Limnogenic Complexes of the Southern Urals (A.A. Rasskazov, I.E. Stukalova, and A.V. Tarasov)

Peculiarities of the Lithologic Structure of the Riphcean-Type Section (L.V. Anfimov)

The Mineral Composition of Diagenetic Carbonate Concretions from Riphean Deposits of the Type Section (A.T. Rasulov)

Peculiarities of Sedimentation and the Dynamics of Formation of the North Uralian Bauxite Basin (V.P. Shatrov)

Lithofluidal Systems in the Sedimentary Basin of the Bashkiria Meganticlinorium (N.I. Kagarmanova)

Riphean Megarhythms and Synchronous Magmatism (V.A. Filippov).

The paper by Timofeev titled *The Role of Sedimentology in Solving Basic Geological Problems of the Early 21st Century* was delivered at the closing phase of the meeting. The bulk of attention was given to the further improvement of the facies method of studying the sedimentary rocks as a basis for elaborating the concept on the genetic sedimentary formations. According to Timofeev, the key problem of the 21st century should be the problem of elaborating "the fundamentals of the theory of the sedimentation process," which is based on the concept of the expanding Earth.

The meeting was a success. The abstracts of all declared papers as well as a routine issue of the UGGGA (scientific thematic collected articles *Geology of Coal Deposits*) were published.

The participants expressed their gratitude to V.P. Alekseev, professor of UGGGA, for the excellent arrangement of the meeting. The idea to hold regular meetings of that sort and to make them traditional was readily approved. The objectives of such meetings could be different theoretical and practical problems of sedimentary geology, the Urals regions included.

P. P. Timofeev, V. P. Alekseev, and L. V. Anfimov

CHRONICLE

The First All-Russia Lithological Workshop of Young Scientists

The First All-Russia Lithologic Workshop of Young Scientists was held within the framework of the Federal Specific Program "The State Support for Integration of Higher Education and Fundamental Science for 1997–2000" (FSP *Integratsiya*) in Melikhovskaya village, Ust'-Donetsk district, Rostov region, from September 29 to October 2, 1998. The workshop attracted 52 specialists from 9 research, educational, and industrial institutions of the Russian Academy of Sciences (RAS), and the Ministry of General and Vocational Education (henceforth, Ministry of Education), the Ministry of Natural Resources of the Russian Federation. The participants included 7 academicians and corresponding members of the Russian Academy of Sciences, the Russian Academy of Natural Sciences (RANS), and the International Academy of Mineral Resources (IAMR), 12 DSc and 19 PhD degree holders in Geological–Mineralogical Sciences.

Co-chairmen of the Workshop Organizing Committee were Prof. P.P. Timofeev from the Geological Institute of the RAS (GIN), corresponding member of the RAS, chairman of the Interdepartmental Lithological Committee of the RAS (ILC), as well as Prof. V.I. Sedletskii, academician of the RANS, vice-chairman of the Council of the North Caucasus Research Center for Higher Education (SKNTS). Scientific Secretary of the workshop was O.S. Ponomarenko, Rostov State University (RGU).

At the opening ceremony, the participants were greeted by Prof. P.P. Timofeev, Prof. N.I. Boiko, academician of the IAMR, and P.P. Ul'yanov, chairman of the Committee for Natural Resources for the Rostov region.

Thirty-four papers were presented at 7 sessions and a geological excursion was carried out during which the participants got acquainted with a geologic section of the Paleozoic and Cenozoic deposits of the eastern Donetsk basin (Donbas).

Key papers were focused on four themes: (1) Fundamentals of sedimentogenesis and lithogenesis, the concept of facies, and the facies analysis; (2) the study of organic matter in sedimentary formations; (3) methods of studying the sedimentary formations and related mineral resources; and (4) the study of metallogeny of sedimentary complexes in the context of new data on their structure, composition, and depositional conditions.

The fundamentals of sedimentogenesis and lithogenesis, the concept of facies, and the facies analysis were considered in presentations by Prof. P.P. Timofeev

(GIN); Prof. V.I. Sedletskii, DSc (SKNTS); Prof. O.V. Yapaskurt, DSc (MGU); V.V. Ereemeev, chief researcher, DSc (GIN); and Assoc. Prof. S.I. S'yan, Novosibirsk State Technical University (NGTU).

The problems of studying the organic matter in sedimentary formations were discussed in papers by Prof. B.A. Sokolov, corresponding member of the RAS (MGU); Prof. V.G. Kuznetsov, DSc, State Academy of Oil and Gas (GANG); Prof. L.Ya. Kizil'shtein, DSc, (RGU); V.S. Vishnevskaya, chief researcher, DSc, Institute of the Lithosphere, RAS (IL); L.I. Bogolyubova, chief researcher, DSc, (GIN); M.S. Afanas'eva, PhD, All-Russia Research Oil and Gas Institute (VNIGNI); Yu.V. Agarkov, Assoc. Prof. (RGU); N.V. Granovskaya, Assoc. Prof. (RGU); and N.V. Pronina, Assoc. Prof. (MGU).

The methods of studying the sedimentary formations and related mineral deposits were considered in papers by Prof. I.A. Bogush, DSc, (NGTU); M.I. Chernenko, Assoc. Prof. (NGTU); B.V. Talpa, Assoc. Prof. (RGU); M.M. Ryshkov, Assoc. Prof. (RGU); V.D. Kotlyar, Assoc. Prof. (RGU); V.N. Volkov, Assoc. Prof. (RGU); A.E. Khardikov, Assoc. Prof. (RGU); and O.S. Ponomarenko, postgraduate student (RGU).

The study of metallogeny of sedimentary complexes in the context of new data on their structure, composition, and depositional conditions was the concern of the papers by Prof. N.I. Boiko, DSc (RGU); Prof. V.N. Trufanov, DSc, (RGU); A.G. Granovskii, Assoc. Prof. (RGU); and E.M. Pushkarskii, Assoc. Prof. (RGU).

Poster papers were presented by postgraduate students and young researchers D.V. Khrupin and A.N. Arkhipov (RGU), A.V. Areshin (GIN), A.V. Sukhov (MGU), D.V. Kurilov (IL), and others. Such form of presenting materials proved to be an effective mode of discussing and exchanging opinions.

Timofeev, Kuznetsov, Boiko, Bogolyubova, Yapaskurt, Vishnevskaya, and other researchers took part in discussions and debates. The participants accepted the elaboration of the concept on the genetic and formational analysis, the concept of facies and facies analysis, and the study of organic matter in the sedimentary process to be among the top priority fields in sedimentology and lithology. The problem of studying carbonate, evaporite, siliceous, clayey, and other formations still remains to be important. The study of metallogeny of sedimentary complexes in the context of new data on their composition, structure, and depositional conditions was considered as necessary.

As a result of four-day work of the workshop, a detailed resolution has been adopted, the principal issues of which are as follows: (1) to organize the Second All-Russia Lithological Workshop for Young Scientists in 1999 devoted to pressing issues in lithology and new methods for the study of sedimentary rocks; (2) to advise institutions of the Ministry of General and Vocational Education and the Russian Academy of Sciences to liven up the theoretical and applied studies in the field of lithology that will undoubtedly encourage the integration of higher education and fundamental science; (3) to consider a wider use of advanced devices and computers as an obligatory requirement for the comprehensive study of sedimentary rocks; (4) to recognize it as expedient for geologic faculties in universities and institutes with lithology departments to set up specialized and optional courses for the comprehensive and purposeful study of laboratory research methods in

lithology. With this aim in view, to apply to the Ministry of Education to take effective measures on providing laboratories in higher educational institutions with the analytical base compatible with modern requirements; and (5) to mount efforts in order to elaborate teaching computer programs in lithology.

The participants expressed their sincere gratitude to the Organizing Committee, the administration of SKNTs, the staff of GIN and RGU, and personally to Drs. V.I. Sedletskii, N.I. Boiko, O.S. Ponomarenko, A.E. Khardikov, T.P. Fedulova, S.V. Levchenko, I.A. Kholodnaya, and Yu.V. Agarkov for organizing and hosting the workshop.

**P. P. Timofeev, A. E. Khardikov,
and O. S. Ponomarenko**

CHRONICLE

In Memory of N.A. Lisitsyna



Nadezhda Aleksandrovna Lisitsyna, a prominent lithologist, geochemist, and mineralogist, DSc (Geol.-Miner.), an assistant and collaborator of Academician N.M. Strakhov, passed away on May 22, 1999 at the age of 77 years old.

Lisitsyna was born in Kursk on April 3, 1923. She finished secondary school with a gold medal in Moscow in 1940 and entered Moscow State Geological Prospecting Institute (MGRI). The beginning of the Great Patriotic War violated a peaceful life in the country; in 1941, Lisitsyna went to the front by her own free will and she enrolled in a battalion of tank fighters to take part in Moscow defence. It was not until July 1943 that she returned to MGRI, successfully completed her studies, and received the degree of engineer-geologist in 1946.

Lisitsyna worked in the Aerological Expedition of the Ministry of Geology for several years; as a head of the geological team, she carried out the geological survey as well as studied mountainous and other hard-to-reach regions of Central Asia (the Turkestan and Alai of Tien Shan, as well the Pamir and Darvaz foothills).

Simultaneously, in 1948, she joined the postgraduate course in MGRI where she began to work on the PhD dissertation under the supervision of Prof. A.A. Bogdanov. She successfully defended the dissertation *Conditions of Formation of the Eastern Alai Ridge in the Late Paleozoic* in 1952 and joined the

Museum of Earth Sciences in the Moscow State University (MGU).

A new page in the scientific life of Lisitsyna opened in 1953; in October, Academician N.M. Strakhov offered her a job at the Geological Institute where she then worked for about 40 years until retirement on a pension in 1992.

During the early years of activity in the Laboratory of Sedimentary Rocks, she studied the composition, regularities of location, and conditions of formation of bauxites in Kazakhstan and Western Siberia. Later, she took an interest in numerous showings of weathering crusts which bauxite deposits are genetically related to. Under the supervision of Strakhov, she studied the dynamics of the formation of the recent (Quaternary) and older weathering crusts of the Caucasian Batumi coast, Vietnam, Ukraine, Kazakhstan, as well as islands of the Pacific and Indian oceans. On the basis of comprehensive mineralogical and geochemical studies of all these complicated objects, she prepared the DSc dissertation *Regularities of the Distribution and Removal of Chemical Elements during Weathering of Basic Rocks* and successfully defended this work in 1969. The book titled *The Removal of Chemical Elements during Weathering of Basic Rocks*, based on the DSc dissertation, was published in 1973. After applying the isovolumetric calculation method in this work, Lisitsyna constructed a quantitative model of weathering of basic and acid igneous rocks in the hypergene zone, distinguished different stages of the process, and estimated the removal intensity and redistribution features of major and minor elements.

Her DSc dissertation is undoubtedly a major contribution to geochemistry of the sedimentation process; it unravels the essence of the most important stage of sedimentation related to the mobilization of substance under weathering in a continental block. Later, the results of the work were widely used by many lithologists, although, the book unfortunately gained no official recognition in due time.

In the late 1960s, Lisitsyna started studying the regularities of the modern sedimentation in seas and oceans. Her pioneer works in this field were carried out under the program elaborated by Strakhov, which dealt with the transpacific lithofacies profile. Along with G.Yu. Butuzova (Geological Institute, RAS) and I.I. Volkov (Institute of Oceanology, RAS), Lisitsyna studied in detail the lithofacies types, the granulometric and mineral compositions, as well as geochemical features of recent sediments in the Pacific along the Japan–

Hawaii–California profile including 100 stations. The observations allowed a quantitative assessment of the mechanism of oceanic lithogenesis to be made.

Later, Lisitsyna gave much attention to studying the authigenic mineral formation in seas and oceans, manganese ore and crusts, and problems of geochemistry of Mn and Fe in water and bottom sediments. She participated in numerous expeditions in the Pacific, Indian, and Atlantic oceans, in the first Russian expedition PIKAR with the use of submersibles in the Red Sea, in processing and generalizing materials of deep sea drilling.

During 46 years of research, Lisitsyna published more than 100 works, including 8 monographs (6 of them were written in collaboration with other researchers). The majority of her papers were published in our journal.

When analyzing the scientific creative power of Lisitsyna, an image of a bright and purposeful woman

comes to mind. She was notable for a great diligence, strictness, aspiration for mastering new methods of research, and an excellent command of the microscopy methods.

In the course of field and sea expeditions, she proved to be a tireless researcher inclined not only to comprehensive processing of the material collected but to sweeping generalization as well.

The death of Nadezhda Aleksandrovna Lisitsyna means that our science undoubtedly suffered a severe loss. She left a fond memory of herself in her works and our hearts.

**The staff of the Geological Institute (GIN),
Russian Academy of Sciences
Editorial Board of the Journal
*Lithology and Mineral Resources***

CHRONICLE

The Centenary of M.P. Fiveg

On September 21, 1999, it was 100 years since Mikhail Pavlovich Fiveg, DSc (Geol.-Miner.), a prominent Russian geologist, well-known specialist in the field of geology, prospecting and exploration for agrochemical ores, was born. All of his scientific and applied activity was devoted to studying apatite and potassium deposits of the former Soviet Union and to organizing and developing the phosphate and potassium industry.

Fiveg was born in the family of the chief engineer of a glass factory in Yashchera village near St. Petersburg. After finishing secondary school in Smolensk, he entered the Moscow Mining Academy and graduated in 1927. In 1924, simultaneously with studying, he began working at the Research Institute of Fertilizers (RIF) under the supervision of A.D. Arkhangel'skii. Since 1926, he was supervising phosphorite-prospecting works in the Orel, Bryansk, and Aktyubinsk regions. These works resulted in the discovery of the Polpin, Dmitrov, and some other phosphorite deposits.

From 1928 to 1938, he was engaged in studying apatite deposits. During that period, he headed the Khibiny Expedition of RIF, supervised the prospecting and exploration, as well as researched the mineralogy and petrography of apatite–nepheline ores. Under his leadership, mineral deposits of top priority were prospected; reserves were estimated; and after reporting the results to S.M. Kirov at the historical meeting in the Khibiny in the New Year Eve of 1930, a decision was made on designing and constructing the Kukisvumchorr mine and the ore-dressing plant.

Fiveg was one of the discoverers of the Khibiny apatite which laid the basis for creating the phosphate industry of Russia. His fundamental research in the field of geology and mineralogy of the Khibiny apatite deposits, as well as conditions of their formation, have gained wide recognition. In 1938, he got his PhD degree in Geological–Mineralogical Sciences without the official defence procedure and, in the same year, he was appointed chief geologist in the Central Board of Chemical Industry (Glavkhimprom).

After joining the All-Union Institute of Halurgy (VIG) as chief engineer in 1940, all of his subsequent activity was related to the geology of salt, to the devel-

opment of which he had made an outstanding contribution.

During the Second World War, Fiveg studied the carnallite zone of the Verkhnekamsk potassium deposit; worked on the stratigraphy, petrography, and tectonics of salt-bearing deposits; took part in estimating the reserves for the first and second mines; and elaborated the procedure of prospecting potassium deposits.

From 1944 to 1946, Fiveg worked at the State Research Institute of Mining and Chemical Raw Materials (GIGKhS) as chief geologist. Until 1968, he worked at the VIG as Head of the Geological Laboratory. Until 1979, he worked as a consultant in the same institute.

Fiveg devoted more than 40 years to studying geology of salt-bearing and potassium deposits. He got acquainted with a great number of potassium deposits of Russia, Ukraine, Belarus, Turkmenistan, as well as Germany and Romania. Based on these materials, he carried out a series of very significant researches into revealing the regularities in the formation of salt-bearing and potassium deposits. He showed that many of the older major halogen basins were not lagoons but sea basins. In detail, he distinguished the characteristic features of the development of halogen zones at the potassium stage of their existence. The results were generalized by him in the dissertation *Geological Environment of the Sedimentation of Salt-Bearing Series and Their Potassium Horizons*. In 1962, he was awarded the DSc (Geol.-Miner.) degree for this work. The work put Fiveg among the leading Russian scientists in the field of geology of salts. During these years, he established cordial and friendly relations with N.M. Strakhov and A.L. Yanshin who shared and supported his views.

It was until his last years that Fiveg carried out intense researches and generalized materials on the geology of salt-bearing basins and conditions of their formation, thus, developing and refining the theory of halogenesis. He was also an active contributor of our journal.

Fiveg belonged to the generation of geologists in this country, to the lot of which a heavy and great but noble challenge fell to provide our economy with mineral raw material under conditions of the fast developing mining industry in the 20th century, as well as to lay the groundwork for scientific prediction of mineral

deposits in the Earth's crust, the foundation for modern theoretical knowledge of conditions of the formation and regularities of distribution of phosphate and salt-bearing formations.

Fiveg was a man of prodigious erudition and culture, as well as a benevolent and responsive person who always shared his experience and knowledge

with other people. During his long life, he trained many disciples who successfully continued his work on studying the apatite-bearing provinces and salt-bearing basins in various regions of Russia and abroad. His work was highly appreciated by our country, and he was awarded the highest orders and medals of the Soviet Union.

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